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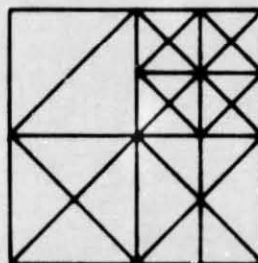
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Technical and Economic Assessment of Processes for the Production of Butanol and Acetone

A Study for
Jet Propulsion Laboratory
Pasadena California



Chem Systems Inc.

Technical and Economic Assessment of Processes for the Production of Butanol and Acetone

This is the Final Report of a Study Effort performed for the United States Department of Energy/Energy Conversion Utilization Technology Office (DOE/ECUT). The work was performed by Chem Systems Inc. under Contract No. 956277 with the Jet Propulsion Laboratory of the California Institute of Technology, sponsored by The National Aeronautics and Space Administration under Contract NAS7-100.

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September, 1982

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FINAL REPORT

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This report was performed as part of the Department of Energy's Energy Conversion and Utilization Technology (ECUT) Program, under the direction of the Jet Propulsion Laboratory.

EXECUTIVE SUMMARY

This report represents a preliminary technical and economic evaluation of a process which produces mixed solvents (butanol/acetone/ethanol) via fermentation of sugars derived from renewable biomass resources. The objective is to assess the technology of producing butanol/acetone from biomass, and select a viable process capable of serving as a base case model for technical and economic analysis. It is anticipated that the base case process developed herein can then be used as the basis for subsequent studies concerning biomass conversion processes capable of producing a wide range of chemicals.

The general criteria utilized in determining the design basis for the process are profit potential and non-renewable energy displacement potential. The feedstock chosen, aspen wood, was selected from a number of potential renewable biomass resources as the most readily available in the United States and for its relatively large potential for producing reducing sugars.

The butanol/acetone/ethanol (ABE) production facility consists of three major sections. These are:

- i) Pretreatment and Enzyme Hydrolysis
- ii) Fermentation
- iii) Purification

The specific design basis for the Pretreatment and Enzyme Hydrolysis section has been derived from recent research in biomass conversion technology as well as previous Chem Systems analyses of work in this area. The design bases for the Fermentation and Purification sections are similar to conventional batch fermentation and conventional butanol/acetone distillation technology presently utilized in the industry. No attempt has been made to improve upon the existing technology in these two sections. However, the important fermentation process parameters; namely, initial sugar concentration, fermentation

time, solvent yield and solvent ratio are representative of empirical data obtained by various researchers for wood or wood sugar feedstocks. It is also important to note that a number of simplifying assumptions have been made in determining the design basis for each of the plant sections. This was necessary in order to fill in the data gaps that presently exist in ABE fermentation technology from wood substrates. These assumptions are discussed in detail in Section I of the report and should be referred to in order for the reader to gain the proper perspective on the study conclusions.

The study considers two separate cases in an attempt to provide some quantitative insight into the sensitivity of overall plant economics to certain fermentation design parameters. The fermentation of wood-derived sugars by *Clostridium acetobutylicum* has a maximum yield at 3 percent initial sugar. This yield begins to decrease as initial sugar concentration is increased beyond 3 percent. At 6 percent initial sugar, microorganism activity falls to zero due to the level of butanol toxicity associated with this sugar concentration (approximately 1.3 percent butanol). Therefore, product yield is maximized at 3 percent initial sugar while product concentration is maximized at 6 percent initial sugar.* The two cases considered are taken at two available data points, one representing the maximum yield case at 3 percent initial sugar, and the other increasing the initial sugar concentration to 5 percent while sacrificing yield. In this way, the maximum yield case gives a result minimizing raw material consumption, while the lower yield case reduces capital and utility requirements in the purification section.

This cursory analysis of fermentation design parameters resulted in significantly lower production costs for the lower yield case. This is shown in Table 1, which is a cost of production summary for the two ABE

* The significance of product concentration is that the higher the solvent concentration in the fermentation beer, the less steam and steam-related capital are required for product purification.

cases analyzed. It can be seen from the table that the mixed solvent product can be produced for 2.83 dollars per gallon for the maximum yield case as compared to 2.58 dollars per gallon for the lower yield case. This result indicates that the process economics are extremely sensitive to changes in capital and utility consumption in the purification section, which is of course directly related to solvent concentration in the fermentation beer.

TABLE 1

SUMMARY OF ABE FERMENTATION PROCESS ECONOMICS

BASIS: 50 MM gals/yr, U.S. Gulf Coast Mid-1982

	<u>Maximum Yield</u>	<u>Lower Yield</u>
Investment, \$\$MM		
Battery limits	96.1	92.8
Offsites	110.4	97.3
Total fixed investment	<u>206.5</u>	<u>190.1</u>
Cost of production, ¢/gal		
Raw materials	75.80	80.26
Utilities	69.17	53.39
Operating costs	14.68	14.28
Overhead expenses	77.70	73.01
Total cost of production	<u>237.35</u>	<u>220.94</u>
By-product credit	(22.27)	(23.20)
Net cost of production	<u>215.08</u>	<u>197.73</u>
Selling price at 10% DCF	282.6	258.0

Upon closer examination of the process economics, it can be seen from Table 2 that if cost of production is broken down by plant section with raw material costs added as a separate entity, the purification section is the single largest contributor to total cost of production in both cases. Purification accounts for 41.6 percent and 36.0 percent of total cost of production for the maximum yield and lower yield cases respectively. Of this, approximately 73 percent is utilities consumption, primarily steam for distillation.

TABLE 2

UTILITY, OPERATING AND OVERHEAD EXPENSES BY PLANT
SECTION AS A PERCENT OF TOTAL COST OF PRODUCTION

Maximum Yield Case - Total COP - 215.08 ¢/gal

<u>Section</u>	<u>COP ¢/gal</u>			<u>Section Total</u>	<u>% Total COP</u>
	<u>Utilities</u>	<u>Operating</u>	<u>Overhead</u>		
Enzyme hydrolysis	1.42	7.94	36.92	46.28	21.5
Fermentation	1.96	4.49	19.23	25.68	12.0
Purification	65.79	2.23	21.50	89.52	41.6
Raw materials (minus by-product credit)				53.53	24.9

Lower Yield Case - Total COP - 197.73 ¢/gal

Enzyme hydrolysis	1.53	8.98	41.71	52.22	26.4
Fermentation	(.3)	3.43	14.34	17.47	8.8
Purification	52.16	1.83	17.18	71.17	36.0
Raw materials (minus by-product credit)				57.06	28.9

A breakdown by plant section of energy consumption in the process reveals, not surprisingly, that the purification section is overwhelmingly the largest consumer of energy. Table 3 shows total energy consumption by plant section, which includes both steam and power but neglects the raw material energy associated with the feedstock. The table indicates that the purification section consumes more than 100 percent of the total plant energy in both cases. This is possible due to the fact that energy is produced at various points in the process which is then allocated to the plant section where it occurs.

TABLE 3
TOTAL ENERGY CONSUMPTION BY PLANT SECTION
 (MMBtu per Year)

Maximum Yield Case

<u>Section</u>	<u>Steam</u>	<u>Power</u>	<u>Section Total</u>	<u>% Total</u>
Enzyme Hydrolysis	(575,559)	340,650	(234,909)	-3.26
Fermentation	(478,634)	675,900	197,266	2.74
Purification	7,236,446	8,950	7,245,396	100.52
Total	6,182,253	1,025,500	7,207,753	100.00

Lower Yield Case

Enzyme Hydrolysis	(652,827)	385,400	(267,427)	-4.98
Fermentation	(521,192)	496,000	(25,192)	-.47
Purification	5,658,698	8,600	5,667,298	105.45
Total	4,484,679	890,000	5,374,679	100.00

In order to compare the relative merits of the ABE fermentation process vis a vis conventional routes to butanol and acetone, an economic analysis of the conventional technologies was performed. Table 4 is a summary of process economics of butanol and acetone via the conventional synthetic route, from propylene. As can be seen from a comparison of Tables 1 and 4, the conventional routes produce butanol and acetone at 2.35 and 2.32 dollars per gallon respectively and have approximately a 10 percent edge over the better ABE case (the lower yield case).

TABLE 4
SUMMARY OF PROCESS ECONOMICS
FOR CONVENTIONAL ROUTES TO BUTANOL AND ACETONE

Basis: 50 MMgals/yr, U.S. Gulf Coast, mid-1982

	<u>Butanol</u>	<u>Acetone</u>
Investment, \$MM		
Battery limits	61.2	41.2
Offsites	28.8	29.2
Total fixed investment	90.0	70.4
Cost of production, ¢/gal		
Raw materials	165.57	135.50
Utilities	5.62	25.84
Operating Costs	9.50	7.10
Overhead expenses	40.10	30.03
Total cost of production	220.80	198.47
By-product credit	(21.25)	(2.34)
Net cost of production	199.55	196.13
Selling price at 10% DCF	235.1	232.4

The conclusions that can be derived from this analysis are apparent. The purification step is the most significant step in the process in terms of total cost of production and energy consumption. In addition, although ABE fermentation from wood is undoubtedly viable technically, it is presently still not competitive with the conventional routes to butanol/acetone via propylene. It is therefore obvious that future research and development in ABE fermentation should focus on reducing the costs and energy consumption associated with the purification step. Specifically, this might be achieved by:

- i) Developing improved separation techniques such as reverse osmosis, membrane separation, solvent extraction, adsorption, etc., which have great potential for reducing energy consumption during ABE purification.

- ii) Developing an improved microorganism via genetic manipulation which can satisfactorily ferment wood sugars and can tolerate high concentrations (greater than 1.3 percent) of butanol in the fermentation beer.

INTRODUCTION AND PERSPECTIVE

This report was prepared as part of the Department of Energy's Energy Conversion and Utilization Technology (ECUT) Program, whose objective is to support long-term, high-risk applied research and development necessary to assure the availability of a future technology base that will enable a substantial increase in both the efficiency of energy conversion and utilization equipment and the increased use of non-critical fuels. It forms a segment of the Chemical Processes Project of the Energy Utilization Technology SubProgram, which focuses on the engineering of biocatalyzed processes for producing chemicals.

The objective of the study is to develop a methodology for analyzing the impact of technological advances as a tool to help establish priorities for R & D options. As an example of a biocatalyzed process, butanol/acetone fermentation (ABE process) was selected as the specific topic of study. For ease of comparison with conventional production plants, a Gulf Coast location was hypothesized. Process economics are based on a size of 50 million gallons per year, as this was deemed to be a reasonable size plant for producing alcohols for the fuel market.

I. DESIGN BASIS

A. Introduction

The production of acetone, butanol and ethanol via fermentation (hereafter called ABE fermentation) has been an established commercial technology since the early 20th century. The original organism, *Clostridium acetobutylicum*, discovered by Chaim Weizmann around 1914, was able to ferment starchy substrates such as corn to butanol, acetone and ethanol. The first ABE fermentation plants were built in Canada and then the United States (Terre Haute, Indiana) during World War I primarily to produce acetone which was important in the manufacture of cordite, a component of small arms ammunition and a propellant for heavy artillery shells. After World War I, DuPont developed nitrocellulose lacquers for the automobile industry, and it was found that butyl acetate was the solvent of choice for this coating system. The U.S. ABE fermentation plants were then started up as a private venture to supply butanol as the raw material for the manufacture of butyl acetate.

Early attempts to develop an organism that would ferment molasses (a less expensive substrate than corn) were unsuccessful, however by 1938 a new organism was developed, *C. saccharo-butyl-acetonicum-liquefaciens*, (Arzberger 1938⁽¹⁾, Carnarius and McCutchan, 1938⁽²⁾) which fermented molasses with satisfactory yields. The advent of the supply of cheap petroleum following World War II caused the abandonment of the traditional routes to many chemicals, including ABE fermentation, by most of the chemical industry in the western world (with the notable exception of South Africa). Synthetic routes to chemicals from petroleum continued to be more economical until the 1970s when the series of petroleum price increases led to renewed interest in fermentation of renewable biomass resources.

B. Raw Materials

Clostridium acetobutylicum, discovered by Chaim Weizmann in 1914, successfully ferments starchy substrates such as corn to butanol, acetone

and ethanol. Typical yields for 8.5 percent corn concentration are approximately 26.5 weight percent based on initial dry corn with a solvent ratio of 60 percent butanol, 30 percent acetone and 10 percent ethanol. In 1938, with the discovery of *C. saccharo-butyl-acetonicum-liquefaciens*, fermentation of molasses was made possible. Typical yields for molasses with a 5.5-7.5 percent sugar concentration are 30-33 percent based on sucrose, with a solvent ratio of 20-35 percent acetone, 61-76 percent butanol and 4 percent ethanol. Fermentation times are typically 50-60 hours for the corn substrate and 40-45 hours for the molasses feedstock. Although other species of microorganisms can be used to ferment corn and molasses, *C. acetobutylicum* and *C. saccharo-butyl-acetonicum-liquefaciens* are the most widely used.

Most of the ABE fermentations heretofore have used one of three carbohydrate sources as a feedstock; namely, corn, blackstrap molasses or high test molasses.* However, when considering the potential of ABE fermentation to replace synthetic petroleum routes to these three chemicals, carbohydrate sources, some of which are normally considered waste products, will be evaluated as potential feedstocks.

This list includes wood and wood wastes, agricultural wastes such as corncobs and corn stover, municipal solid waste (MSW), whey, and sulfite liquor. Each of these carbohydrate sources would be a feasible feedstock for ABE fermentation, however, a selection of the most suitable substrate will be made based upon the best available information.

The best feedstock for ABE fermentation must have certain characteristics which will enable the process to be both technically and economically

* Blackstrap molasses is the concentrated mother liquor from the crystallization of sugar cane juice and contains 50-55% sucrose. High test molasses is the concentrate of sugar cane juice of which 67% of the sucrose has been inverted to glucose and fructose to avoid crystallization and sugar import duties.

viable. The feedstock must be abundantly and inexpensively available in the United States, and must have a high potential for conversion to products with a minimum of complicated or expensive processing steps required. In general, wood has a very high potential for conversion to sugar, and ultimately to solvents, and is readily and abundantly available in the United States. In addition, considering recent advances in the technology of wood hydrolysis, high yields of wood to fermentable sugars can be obtained with relatively good economics. (See Pretreatment Enzyme Hydrolysis, Section C.)

Wood is composed of several major carbohydrate fractions which comprise the bulk of the cell wall. In addition, a small fraction of wood consists of extraneous materials, which are both organic and inorganic. The carbohydrate fraction of wood consists primarily of cellulose, hemicellulose and lignin. Cellulose is composed entirely of six carbon sugars (hexosans) while hemicellulose is a mixture of five (pentosan) and six carbon sugars. Lignin is a complex amorphous aromatic substance composed of cross-linked polymers of phenylpropanoid units joined by benzylic and phenolic ether linkages. In addition, a small fraction of wood is composed of extraneous materials such as ash (mineral salts), resin and volatile acids, oils, polysaccharides and other miscellaneous organic materials.

Cellulose is a homogeneous polymer of glucose, while hemicellulose can be a conglomeration of polymers of hexoses (glucose, galactose and mannose) and pentoses (xylose and arabinose). The specific composition of wood varies from species to species. Table I-B-1 shows the typical composition of several woods. It can be seen from the table that, in general, hardwoods have a greater holocellulose (cellulose and hemicellulose) content than softwoods, although the hexosan content is approximately equivalent for both, due to a lower percentage of xylans in the softwood hemicellulose. However, the main hexosan component of softwood is mannan (mannose), which although fermentable, has a much

slower fermentation rate when compared to glucan (glucose). In addition, softwood susceptibility to enzyme hydrolysis is virtually unchanged when subjected to various pretreatments.

TABLE I-B-1
PERCENTAGE COMPOSITION OF CERTAIN WOODS
(Extractive Free, Ash Free)

	<u>Lignin</u>	<u>Holo- cellu- lose</u>	<u>Alpha- cellu- lose</u>	<u>Hemi- cellu- lose</u>	<u>Pento- sans</u>	<u>Uronic acid anhy- dride</u>	<u>Acetyl</u>	<u>Methoxyl in Carbohy- drate</u>
Softwoods								
White Spruce	26.6	73.3	49.5	23.8	10.9	2.68	2.35	0.70
Red Spruce	26.6	72.9	48.3	24.6	11.6	3.20	2.50	0.92
Eastern Hemlock	31.5	68.5	48.2	20.3	10.0	3.40	1.87	0.81
Balsam Fir	30.1	69.9	44.0	25.9	10.3	3.08	2.24	0.41
Jack Pine	27.2	72.5	49.5	23.0	12.8	2.92	1.92	0.75
Hardwoods								
Aspen	17.3	82.5	50.7	31.8	23.5	4.28	4.65	0.93
Willow	22.0	78.3						
Maple	23.5	76.3	50.0	26.3				
White Oak	24.1	75.4	49.5	25.9				

Table I-B-2 indicates the potential reducing sugars that can be produced from hardwoods and softwoods. It shows that aspen has the greatest potential for producing reducing sugars which can subsequently be fermented. Populus Tremuloides (poplar) or trembling aspen has high availability in North America and can be grown as a high yield, short rotation crop in many parts of the northern United States. These reasons make aspen an excellent feedstock for the conceptualized ABE fermentation process described herein.

C. Pretreatment and Enzyme Hydrolysis

Over 150 years ago it was discovered that wood and other cellulosic materials could be converted to fermentable sugars by heating in the presence of mineral acids. Much effort has been expended since that time

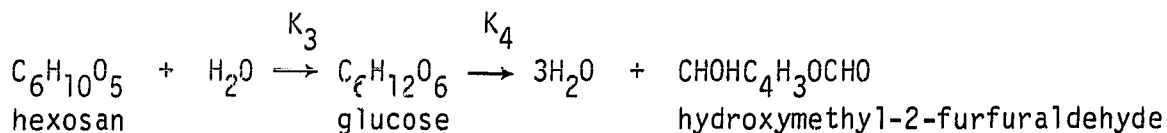
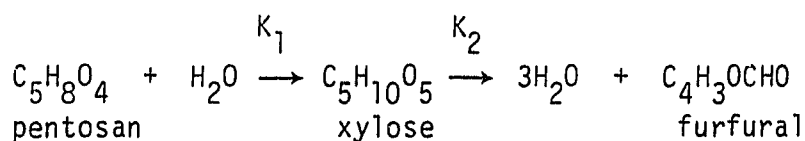
TABLE I-B-2YIELD OF POTENTIAL REDUCING SUGARS AND FERMENTABLE SUGARS
FROM SAMPLES OF REPRESENTATIVE HARDWOODS AND SOFTWOODS

	<u>Potential Reducing Sugars, %</u>	<u>Ferment- ability, %</u>	<u>Potential Fermentable Sugars, %</u>
Hardwoods			
American Beech	70.1	75.1	52.6
Aspen	75.1	76.3	57.3
Birch	69.9	67.8	47.4
Maple	68.2	71.0	48.4
Red Oak	63.6	63.0	40.2
Sweetgum	66.4	73.8	49.0
Yellow Poplar	70.9	76.1	54.0
Softwoods			
Douglas Fir	66.6	86.2	57.4
Eastern White Pine	66.5	86.3	57.4
Hemlock	66.1	88.2	58.3
Ponderosa Pine	68.0	82.2	55.9
Redwood	52.4	77.1	40.4
Sitka Spruce	70.1	85.3	59.8
Southern Yellow Pine	64.8	82.0	53.2
Sugar Pine	64.8	82.4	53.0

in attempts to develop a viable acid hydrolysis process. This effort has been especially intense in the U.S. in recent years following the oil crisis of 1973. The problem with acid hydrolysis is simple; although it was once considered to be the most economically attractive route to producing fermentable sugars from biomass, it has never been economically competitive with conventional routes. Moreover, recent advances in pretreatment for enzyme hydrolysis and enzyme production have currently made acid hydrolysis an unlikely candidate for future consideration as a biomass conversion process.

The technical problems associated with acid hydrolysis are linked to the kinetics of sugar formation and degradation, and the nature of the wood substrate. Wood is essentially composed of three hydrolyzable fractions, hemicellulose, amorphous cellulose and crystalline cellulose. The hemicellulose and amorphous cellulose are easily hydrolyzed to sugar

under mild temperature conditions. The crystalline cellulose is more resistant and requires much higher temperatures. The kinetics of hydrolysis are such that sugar is formed via the hydrolysis of the pentosan (five carbon) and hexosan (six carbon) content of the hemicellulose and cellulose. However, under the reaction conditions of hydrolysis, these sugars are degraded to by-products as a function of temperature and reactor residence time. This is illustrated by the following equations.



Since degradation of sugar occurs immediately following its formation, the ideal situation for high yields is a very high temperature coupled with extremely short residence times. This can be accomplished relatively efficiently with the hemicellulose and amorphous cellulose fractions, since they hydrolyze almost instantaneously to sugars under mild acid and temperature conditions. The mild conditions of this hydrolysis prevent significant degradation to by-products as long as residence times are very short. This hydrolysis (called prehydrolysis) can yield 95 percent conversion of the amorphous cellulose and hemicellulose hexosans and pentosans to glucose and xylose at conditions of 190°C, 0.5 weight percent sulfuric acid and 12 second residence time. However, this is not the case with the crystalline cellulose fraction. Being much more resistant to hydrolysis, much higher temperatures and acid concentrations (230°C, 1.0 weight percent H₂SO₄) are required for conversion. This leads to much greater degradation of the amorphous and hemicellulose sugars which are formed almost instantaneously. If hydrolysis of both amorphous and crystalline

fractions are carried out under the harsher conditions necessary to convert crystalline cellulose, a maximum yield of 50-55 percent can be obtained.⁽³⁾ (Residence time is approximately 12 seconds which is considered a minimum with current extruder-type plug flow reactors.) A scheme to possibly alleviate these problems would be a two-stage hydrolysis. The first stage (prehydrolysis) would be under mild conditions and would recover up to 95 percent of the amorphous cellulose and hemicellulose sugars. These sugars would be separated from the crystalline cellulose which would then undergo hydrolysis under harsher conditions. Overall yields of glucose of 60-70 percent can be obtained for this two-stage process, however, due to the extremely high expense associated with capital and steam consumption of this process, it does not appear to be economically attractive.

Recent advances in enzyme technology, specifically in enzyme productivity, have made enzyme hydrolysis a more attractive route for cellulose conversion than acid hydrolysis. Steam pretreatment of cellulose substrates and mild acid prehydrolysis have enabled glucose yields via enzyme hydrolysis to approach theoretical in a relatively short residence time of around 24 hours. Enzyme production costs, once prohibitively high, have been markedly decreased recently by significant increases in enzyme productivity utilizing new mutant strains of the fungus, T. Reesei.

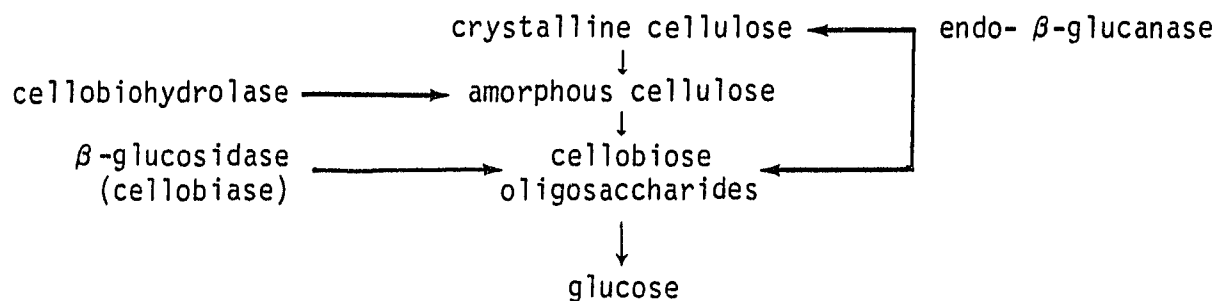
Genetic researchers at Rutgers University⁽⁴⁾ have developed a mutation of T. Reesei, RUT-C-30, which has significantly higher enzyme productivity than the previously used strain, QM9414. In addition, experimentation with various types of nutrient media for enzyme production has enabled cheaper ingredients, such as corn steep liquor and steam exploded wood, to be substituted for the more expensive ingredients previously used such as proteose peptone and delignified cellulose.

The mechanism of enzyme hydrolysis by T. Reesei enzymes occurs when crystalline cellulose is attacked by the enzymes endo- α -glucanase and cellobiohydrolase forming oligosaccharides, including cellobiose. The

cellobiose is then acted upon by endo- β -glucanase and β -glucosidase to form glucose. This is represented in Figure I-C-1.

FIGURE I-C-1

MECHANISM OF ENZYME HYDROLYSIS
by T. Reese¹

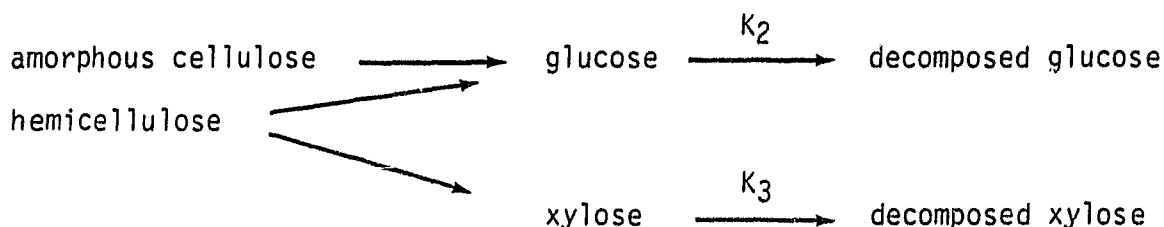


Therefore the enzyme mixture necessary to obtain optimum saccharification is a complex mixture of several enzymes in various proportions. RUT-C-30 has high enzyme productivity, but produces essentially all endo- β -glucanase with little β -glucosidase. Natick labs⁽⁵⁾ has experimented with various mutant strains and has developed QM329 from *Aspergillus phoenicis*, which produces β -glucosidase at very high productivities. Ideally, the optimum enzyme mixture would be a combination of endo- β -glucanase from RUT-C-30 and β -glucosidase from QM329 in a ratio of cellulase:cellobiase of 2:1. However, the preliminary design of the enzyme hydrolysis section is based upon utilizing only RUT-C-30 to produce the enzyme complex.

The preliminary design of the ABE fermentation facility utilizing an aspen wood feedstock will include an acid prehydrolysis pretreatment step and an enzyme hydrolysis and enzyme production step for the processing of wood to the fermentable sugars, xylose and glucose. The use of the acid prehydrolysis pretreatment instead of steam explosion pretreatment is to maximize conversion of the pentosan fraction of the wood to fermentable xylose. As previously mentioned, sugar conversion during prehydrolysis

is approximately 95 percent while, during steam explosion, the high temperatures involved cause significant degradation of the hemicellulose sugars formed. Acid prehydrolysis as a pretreatment has been shown to be nearly as effective as steam explosion, in terms of enzyme hydrolysis yields.

The hydrolysis of amorphous cellulose and hemicellulose is essentially instantaneous to glucose and xylose above 180°C (356°F) and follows a first-order decomposition of the respective sugars:

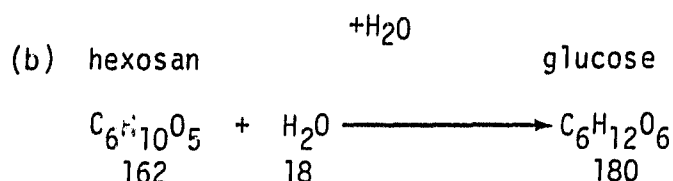
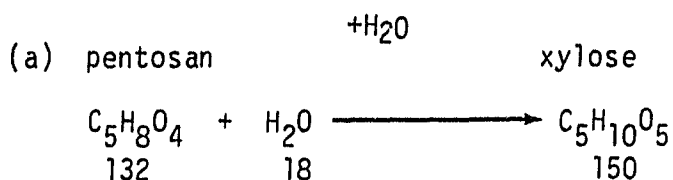
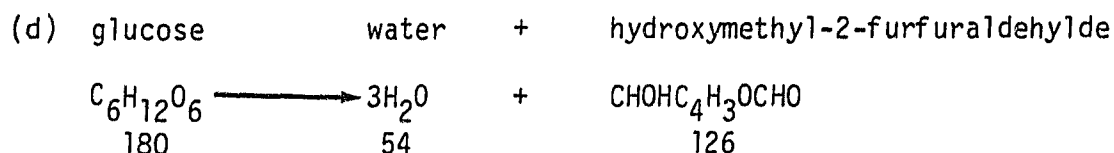
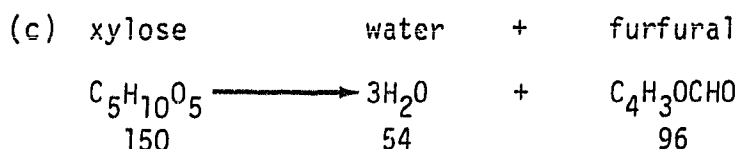


In order to minimize decomposition of the sugars to by-products, and prevent hydrolysis of crystalline cellulose, residence time must be kept as short as is physically possible and temperature and acid concentration must be the minimum required for instantaneous conversion to sugars.

Experimental kinetic studies⁽⁶⁾ performed on various biomass feedstocks have obtained essentially quantitative yields of hemicellulose and amorphous cellulose to xylose and glucose in a plug flow type reactor. Reactor conditions are 0.5 percent sulfuric acid, residence time of 12 seconds and a temperature of 190°C . The preliminary design of the dilute acid prehydrolysis section is developed from the following parameters and assumptions:

Assumptions:

- All hemicellulose is converted to pentoses, hexoses and degradation products according to the following reactions:

Sugar FormationSugar Degradation

- From the kinetics developed by Grethlein⁽⁷⁾ for the conditions of prehydrolysis, 95 mol percent conversion of hemicellulose and amorphous cellulose is obtained almost instantaneously. The remaining 5 mol percent goes to degradation products.
- The amorphous cellulose, which constitutes approximately 15 percent of the total cellulose, is converted to glucose and degradation products in accordance with the same kinetics and conversions as the hemicellulose.

The following parameters and assumptions have been used in the design of the enzyme hydrolysis section. These have been derived from various

research work being conducted at Rutgers University, University of California at Berkeley, Natick Labs and Dartmouth University.

(1) Enzyme Fermenters Design Parameters

- Temperature: 860F
- pH: 4.8
- Pressure: Atmospheric
- Nutrients: 1 percent cellulose
0.2 percent KH_2PO_4
0.03 percent CaCl_2
0.03 percent $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
1 percent corn steep liquor
- Oxygen: 17,264 IU/mol O_2
- Cell concentration: 7 gms/liter
- Cell yield: 0.26 gms mycellium/gm cellulose
- Enzyme yield: 1.63 gms enzyme/gm cellulose based upon enzyme productivity of 114 IU/L/hr
- Cell recycle: 0.77 gm/gm cells

(2) Enzyme Hydrolysis Design Paramters

- Temperature: 1220F
- pH: 4.8
- Pressure: Atmospheric
- Hydrolysis time: 24 hours
- Hydrolysis conversion: 90 mol percent conversion and cellulose to glucose
- Terminal glucose concentration: 5.4 wt %
- Enzyme loading: 12.5 IU/gm cellulose

Assumptions

- Nutrient chemical requirements use cellulose and corn steep liquor concentration as per Rutgers data⁽⁸⁾ and the ratio of other nutrients to cellulose as per Berkeley data.⁽⁹⁾
- Mycellium growth rate is the same for RUT-C-20 as for QM9414 for the same T. Reesei concentration of 7 gms/liter as per Berkeley data.⁽¹⁰⁾
- T. Reesei concentration as per Berkeley data.⁽¹¹⁾

- No xylose or net cellobiose is formed.
- All cellulose consumed forms glucose.
- Enzyme hydrolysis yield, residence time and enzyme loading as per Dartmouth University data.⁽¹²⁾

It is important to note the limitations of the data base for the design of the prehydrolysis, enzyme hydrolysis and enzyme production sections of the facility. The process envisioned is a speculative one which has its basis in data accumulated during bench scale research at the universities noted. Various process steps such as the separation of the lignocellulosic solids from the sugars and solids handling have not been well defined even on a bench scale, and Chem Systems has used its experience and judgement to make assumptions defining the performance of these operations. In addition, it has been assumed that a plug flow reactor (PFR) utilized during prehydrolysis will be similar in design and cost to a Stake type reactor, currently under development by Stake Technology, Inc. of Ottawa, Canada. This reactor presently cannot control residence time down to the 12 seconds prescribed herein, however, it is thought that in time development will enable this lower limit to be obtained. The remainder of the design basis used in the prehydrolysis, enzyme hydrolysis and enzyme production sections of the plant are consistent with empirical data and are judged to be excellent estimates of performance of the various plant sections.

D. Fermentation

Although ABE fermentation has been most widely practiced in the past, utilizing molasses or corn as the feedstock, some research has been conducted on ABE fermentation of sugars derived from wood or agricultural wastes.

Leonard and Peterson⁽¹³⁾ fermented sugar solutions derived from the hydrolysis of various woods with *C. acetobutylicum* to give solvent yields

of 24.5-38.5 percent based on sugar utilized. Sugar utilization was 30-85 percent with solvent yields of 72 percent butanol, 25 percent acetone and 3 percent ethanol. However, yields began to decrease when the initial sugar concentrations exceeded 3 weight percent.

Wiley et al.⁽¹⁴⁾ was able to ferment sugars present in waste sulfite liquor after first removing sulfites, lignin and excess calcium salts. Yields of 25-30 percent were obtained based upon 80 percent sugar utilization. The solvent ratio was 75 percent butanol, 20 percent acetone and 5 percent ethanol. However, waste sulfite liquor suffers the disadvantage of only containing 1-3 percent sugar in the initial feed.

Langlykke et al.⁽¹⁵⁾ fermented to butanol and acetone a glucose and xylose solution obtained from acid hydrolysis of corncobs. An initial sugar concentration of 5 percent gave a solvent yield of 30.6 percent based upon 90 percent sugar utilization. The ratio of solvents was 61.8 percent butanol, 31.8 percent acetone and 6.5 percent ethanol.

Soni et al.⁽¹⁶⁾ was able to ferment sugars obtained from the enzyme hydrolysis of bagasse and rice straw with *C. saccharoper butylaceticum*. Using a 6 percent sugar solution, yields of 33.7 percent were obtained based on 90 percent sugar utilization after 60 hours. The advantage of using *C. saccharoper butylaceticum* is that this microorganism produces a greater fraction of butanol compared to *C. acetobutylicum*. The solvent ratio obtained was 81.3 percent butanol, 12.6 percent acetone and 6.1 percent ethanol.

Abou-Zeid et al.⁽¹⁷⁾, in a study comparing the effect of varying feedstocks on solvent yield, found that a 3 percent glucose solution gave a 32 percent yield on 97 percent sugar utilization after a 72 hour fermentation time. The solvent ratio obtained was 78 percent butanol and 22 percent acetone.

Although none of the above research efforts precisely matches the conditions of the base case chosen for this study, certain generic assumptions can be made concerning ABE fermentation of glucose/xylose

sugar solutions obtained from lignocellulosic substrates. The major problem associated with ABE fermentation of lignocellulosics is the same as that encountered with molasses or corn feedstocks; namely, the microorganisms used cannot tolerate a butanol concentration of greater than approximately 1.3 percent. This translates to a total solvent concentration of approximately 2 percent in the fermentation beer, and an initial sugar concentration of 6 percent. Such low concentrations of solvent in the beer require large amounts of steam and steam-related capital for recovery. However, based upon the results of the research conducted on lignocellulosic substrates, solvent yields begin to decrease at initial sugar concentrations greater than 3 percent. This means that in order to maximize yield, a maximum of 3 percent initial sugar is required. This gives approximately a 1 weight percent total solvent concentration in the fermentation beer which exacerbates the problem associated with low solvent concentrations. In order to obtain the optimum initial sugar concentration, a sensitivity analysis must be performed to determine the effect upon process cost of production (COP) of increasing sugar concentration coupled with decreasing solvent yield.

The base case analysis for this study will consider two points for the ABE fermentation process; one maximizing yield at low sugar concentration, and the other at a higher sugar concentration with a corresponding decrease in solvent yield. Both points will be correlated to empirical data for similar systems.

The maximum yield case essentially follows most of the data of Abou-Zeid et al. obtained for glucose solutions. High sugar utilization of 97 percent is obtained due to the long residence time of 72 hours, giving approximately a 32 percent yield on total initial sugar. An initial sugar concentration of 3 percent is used giving a solvent ratio of 72 percent butanol, 25 percent acetone and 3 percent ethanol.

The higher initial sugar concentration case follows closely the data of Langlykke obtained for ABE fermentation of sugars (xylose/glucose) derived from corncob hydrozylate. A 5 percent initial sugar concentration gives a yield of 30.6 percent on 90 percent sugar

utilization after 48 hours fermentation time. This gives an overall yield on total sugar of 27.54 percent, with a solvent ratio of 61.7 percent butanol, 31.8 percent acetone and 6.5 percent ethanol.

Generic nutrient media for *C. acetobutylicum* and fermentation have been assumed based upon conventional technology. Corn is an excellent growth medium for *C. acetobutylicum* culture maintenance and requires no additional nutrients. Corn for culture maintenance is used in concentrations of 5-5.5 weight percent dry corn. Nutrient media requirements for fermentation are based upon research by Abou-Zeid et al., which studied the effect of varying nitrogen sources and concentration upon ABE fermentation yields. It was found that ammonium sulfate, a relatively inexpensive chemical, was a satisfactory nitrogen source at a concentration of 0.1 weight percent (1 gm/liter). The remainder of the fermentation nutrient requirements are 0.2 percent calcium carbonate and 0.2 percent superphosphate

The following tables list the process parameters used as the design basis for the fermentation section of the facility for both cases considered.

Fermentation Design Parameters

	<u>Maximum Yield</u>	<u>Low Yield</u>
Temperature (°C)	33	33
Initial pH	6.5	6.5
Final pH	5.6	5.6
Residence Time (hours)	72	48
Initial Sugar Concentration (wt %)	3	5
Sugar utilized (%)	97	90
Yield (total sugar) (%)	32	27.54
Solvent Ratio - butanol (%)	72	61.7
acetone	25	31.8
ethanol	3	6.5
Media (wt %) - (NH ₄) ₂ SO ₄	0.1	0.1
superphosphate	0.2	0.2
CaCO ₃	0.2	0.2
Cell yield (gm per gm sugar consumed)	0.5	0.5
Off gas generated per lb sugar consumed (ft ³)	5	5
Off gas composition (%) - CO ₂	67	67
H ₂	33	33

It should be emphasized that there are severe limitations with the basis for the design of the fermentation section. Empirical data on ABE fermentation using a wood substrate is limited, and certainly no optimum design parameters for the specific system analyzed in this study have been developed. The base cases use conventional batch fermentation technology and the conventional microorganism, *C. acetobutylicum*, both of which have been widely used in commercial ABE applications. Research and development in several areas of ABE fermentation could lead to significant improvements in process economics. The problem of low solvent concentration in the fermentation beer could be alleviated by genetic manipulation of microorganisms to develop a species that can tolerate higher butanol concentrations. This could significantly decrease the energy consumption of the solvent purification step, which is one of the most costly steps in the process. In conjunction with this, new microorganisms could be developed to increase sugar utilization and yield improved fermentation rates, and to manipulate the solvent ratio to make more butanol, a higher value product than the other solvents. Also, continuous fermentation using massive inoculum of microorganisms could significantly increase fermentation productivity from a given volume.

E. Purification

The design basis for the solvent purification section is based upon conventional commercial technology. It is sufficient to say that the purification step is by far the most energy-intensive step in the process and directly contributes a large fraction of the total cost of production. As mentioned in the previous section, the low solvent concentration in the feed beer to purification necessitates large steam requirements. Any increase in solvent feed concentration would significantly decrease steam requirements and thus advantageously affect process economics. If increasing solvent feed concentration is not possible, research and development of new, more efficient separation techniques is an alternative. A distillation scheme similar to the state of the art system used in ethanol separation utilizing an efficient heat

recovery scheme could probably reduce purification energy requirements slightly. However, the great promise of a low energy intensive separation technique lies with new separation technologies such as membrane separation, reverse osmosis, solvent extraction, adsorption, etc.

II. PROCESS DESCRIPTION

A. Prehydrolysis

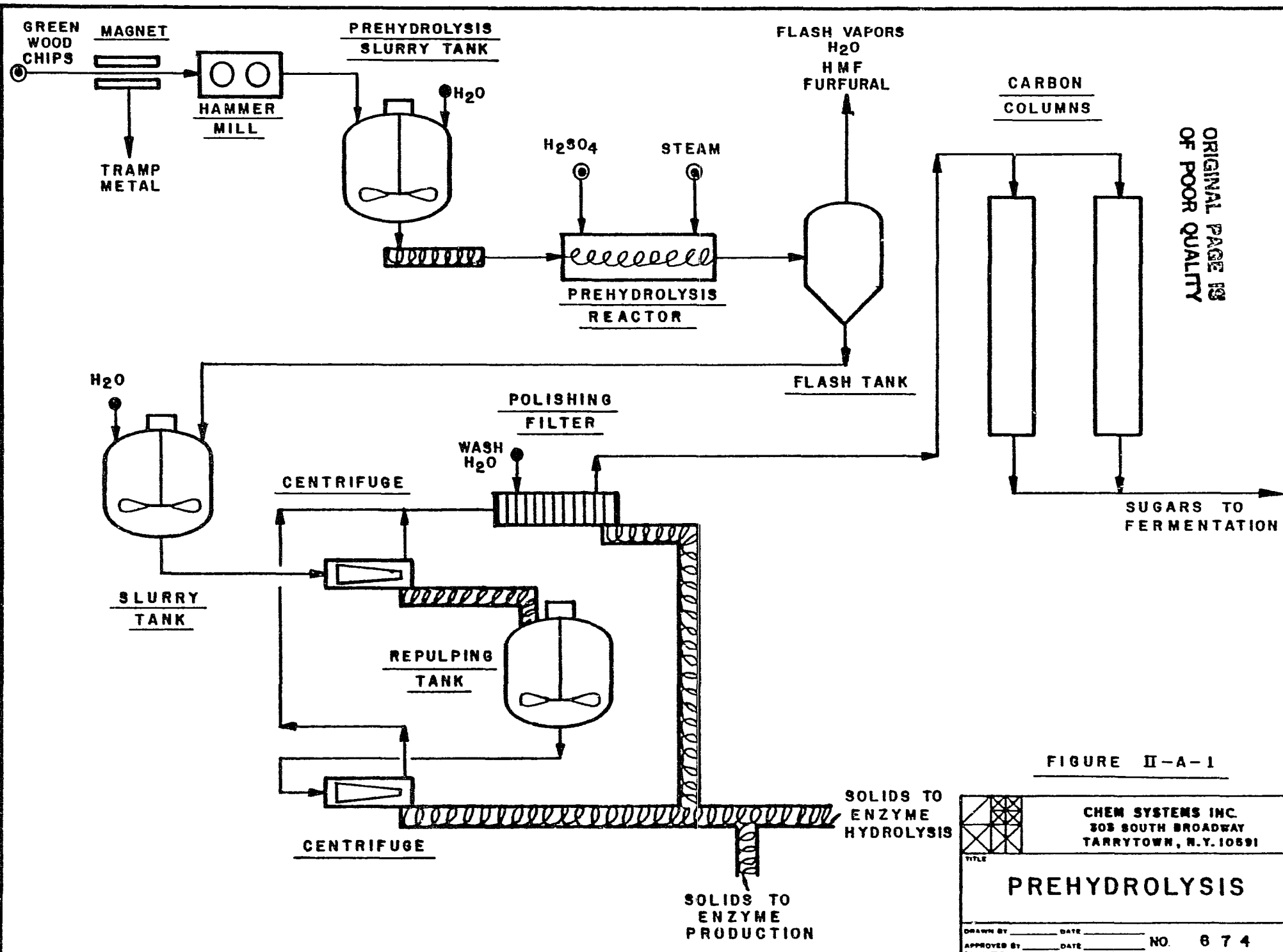
A process flow diagram of the dilute acid prehydrolysis section is presented in Figure II-A-1.

Green wood chips, which contain 50 percent moisture, are conveyed past a magnet, which removes any tramp metal, and sent to a hammer mill. The hammer mill reduces the particle size of the chips which are then sent to the prehydrolysis slurry tank. In the prehydrolysis slurry tank the wood is slurried to 35 percent solids and screw conveyed to the prehydrolysis plug flow reactor (PFR). Heat and sulfuric acid are added in the PFR to bring the reactor conditions to 374°F and 0.5 weight percent acid. Under these relatively mild conditions virtually all the hemicellulose and amorphous cellulose are converted to sugars almost instantaneously. Pressure in the reactor is controlled at 180 psia so that no boiling occurs, and upon leaving the PFR the contents are quenched to 212°F in a flash tank. Some of the water and volatiles (HMF and furfural) are flashed, leaving the unreacted solids and water solubles to be sent to a series of centrifuging steps. Approximately 99 percent of the solids are recovered, including insoluble cellulose and lignin, which are sent to enzyme hydrolysis. A small fraction of this solids stream is sent to enzyme production to serve as the carbon source for enzyme growth. Approximately 95 percent of the solubles including the hemicellulose and amorphous cellulose xylose and glucose are recovered and sent to carbon beds to remove impurities, especially furfural and HMF. The purified sugar stream with a sugar concentration of 5.2 percent is then sent to fermentation.

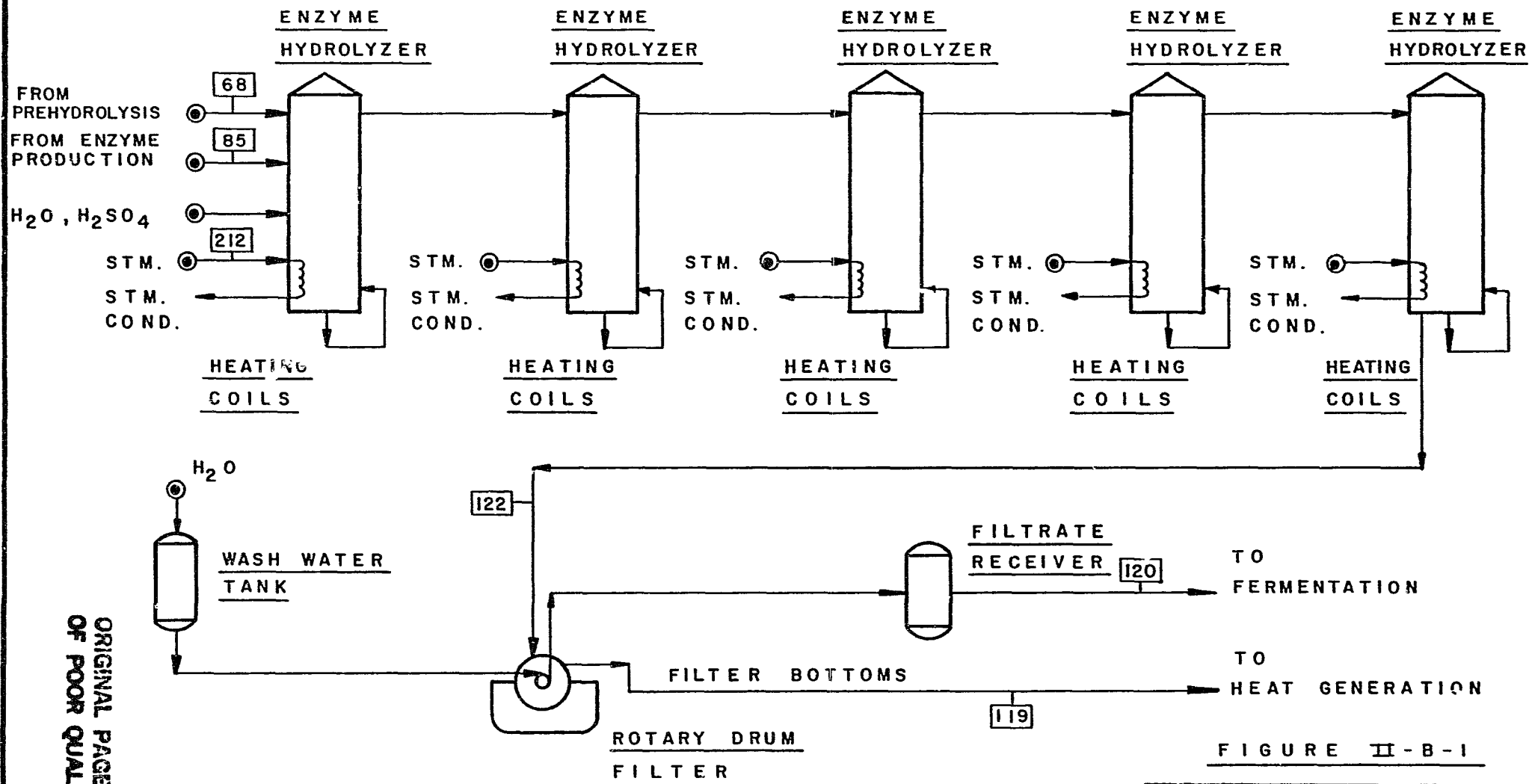
B. Enzyme Hydrolysis

Figure II-B-1 provides a flow diagram for the enzyme hydrolysis section.

The cellulose from pretreatment is slurried to eight weight percent (8 wt. %) solids in the enzyme hydrolyzers and cellulase is added from the



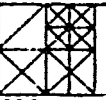
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TEMPERATURE °F

FIGURE II-B-1

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	ENZYME HYDROLYSIS	
DRAWN BY _____ APPROVED BY _____	DATE _____ DATE _____	NO. 6 7 4

enzyme receiver at a loading at 12.5 IU per gram of cellulose. Enzyme hydrolysis is carried out at 122°F and a pH of 4.8. The hydrolyzers are cone-roof, atmospheric tanks with heating coils to maintain the temperature at 122°F. Agitation is provided by recirculation pumps.

A continuous cascade is used for hydrolysis. Two trains of five tanks each are in operation at all times, with one train down for cleaning. Hydrolysis yield is 90 mol percent cellulose to glucose with a total residence time of 24 hours. The sugar solution contains lignin and some unconverted cellulose which is filtered and washed, removing the bulk of the unconverted cellulose. The lignin and unconverted cellulose is concentrated and burned as fuel. The filtrate, containing a glucose concentration of 5.4 percent, is pumped to fermentation.

C. Enzyme Production

A process flow diagram of the Enzyme Production section is presented in Figure II-C-1.

Enzymes for enzyme hydrolysis of cellulose are produced from a mutation of T. Reesei fungus, RUT-C-30. The RUT-C-30 is used as a seed to produce an enzyme mixture of endo-glucanase and β -glucosidase, and also to produce more cells (mycellium). Enzyme production takes place in a two-stage continuous fermentation system at 86°F and a pH of 4.8. Ligno-cellulose from the process is used as a carbon source, corn steep liquor is used as a nitrogen source and other inorganic salts are provided to complete the nutrient requirements. Air is sparged into the fermenters as an oxygen source. Recirculation pumps provided agitation in the vessels and temperature is maintained by steam heated coils.

Carbon dioxide and nitrogen are vented to the atmosphere. The product from the enzyme fermenters is sent to a cell centrifuge to remove most of the mycellium as the centrifuge bottoms. The bottoms are then repulped to eight percent (8 wt. %) solids and filtered and washed to recover the enzyme remaining on the original cake. The cake is split into two streams, one is recycled back to the enzyme fermenters to serve as the enzyme seed, the other is recovered as single cell protein by-product. The centrifuge overflow and filtrate are sent to the enzyme hydrolyzers.

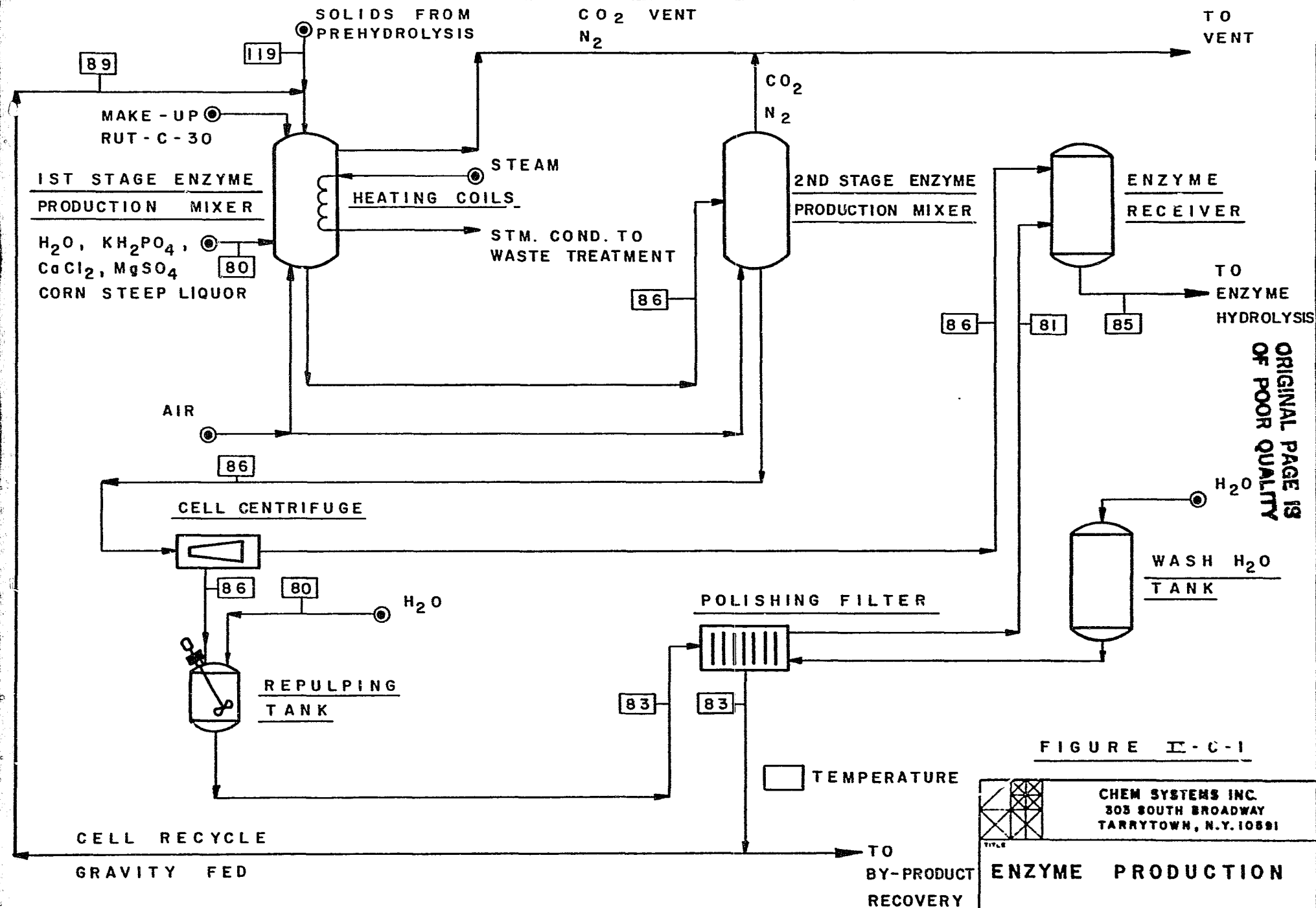


FIGURE II-C-1

<p>CHEM SYSTEMS INC. 303 SOUTH BROADWAY TARRYTOWN, N.Y. 10591</p>	
<p>ENZYME PRODUCTION</p>	
<p>TITLE</p>	<p>NO. 6 7 4</p>
<p>DRAWN BY _____</p>	<p>DATE _____</p>
<p>APPROVED BY _____</p>	<p>DATE _____</p>

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D. Fermentation

Figure II-D-1 is a process flow diagram for the fermentation section.

The sugar stream from prehydrolysis is neutralized with Ca(OH)_2 and filtered to remove the CaSO_4 formed and other residual solids in the stream. The prehydrolysis sugar stream is cooled to fermentation temperature and combined with the hydrolysis sugar stream, which has been passed through carbon beds to remove impurities. The combined sugar stream is sent to batch fermentation vessels where nutrients are added and fermentation to product occurs.

C. acetobutylicum culture development is carried out in three generations in the laboratory and a plant seed stage. All culture development stages use corn as the nutrient media. The first generation is inoculated with a stock culture "heat shocked" in boiling water and incubated at 37°C for 24 hours. Sterile conditions are always maintained in each growth stage by use of steam. The first generation inoculum is used to inoculate the second generation which is then used to inoculate the third generation. Incubation conditions are similar for all three generations. The plant seed stage is inoculated with third generation seed and sterilized corn, and incubated for 26-28 hours during which careful measurements are made to monitor pH, aerobic contamination and gas rates. If the aerobic contamination test is negative, the seeds are used to inoculate the fermenter vessels.

The fermentation vessels are cone roof tanks 1-2 million gallons capacity each depending upon which of the two fermentation cases is considered. The fermentation nutrient media, $(\text{NH}_4)_2\text{SO}_4$, superphosphate and CaCO_3 , are sterilized in cookers, cooled to 33°C and added to the fermentation vessel along with the seed inoculum, slopback and sugar solutions during the fill period. A slightly positive pressure of sterile fermenter gas is maintained on the fermenters during the filling period (2-3 psig) which is increased to 10-15 psig after filling and maintained at this value by the gas evolved during fermentation. Heat

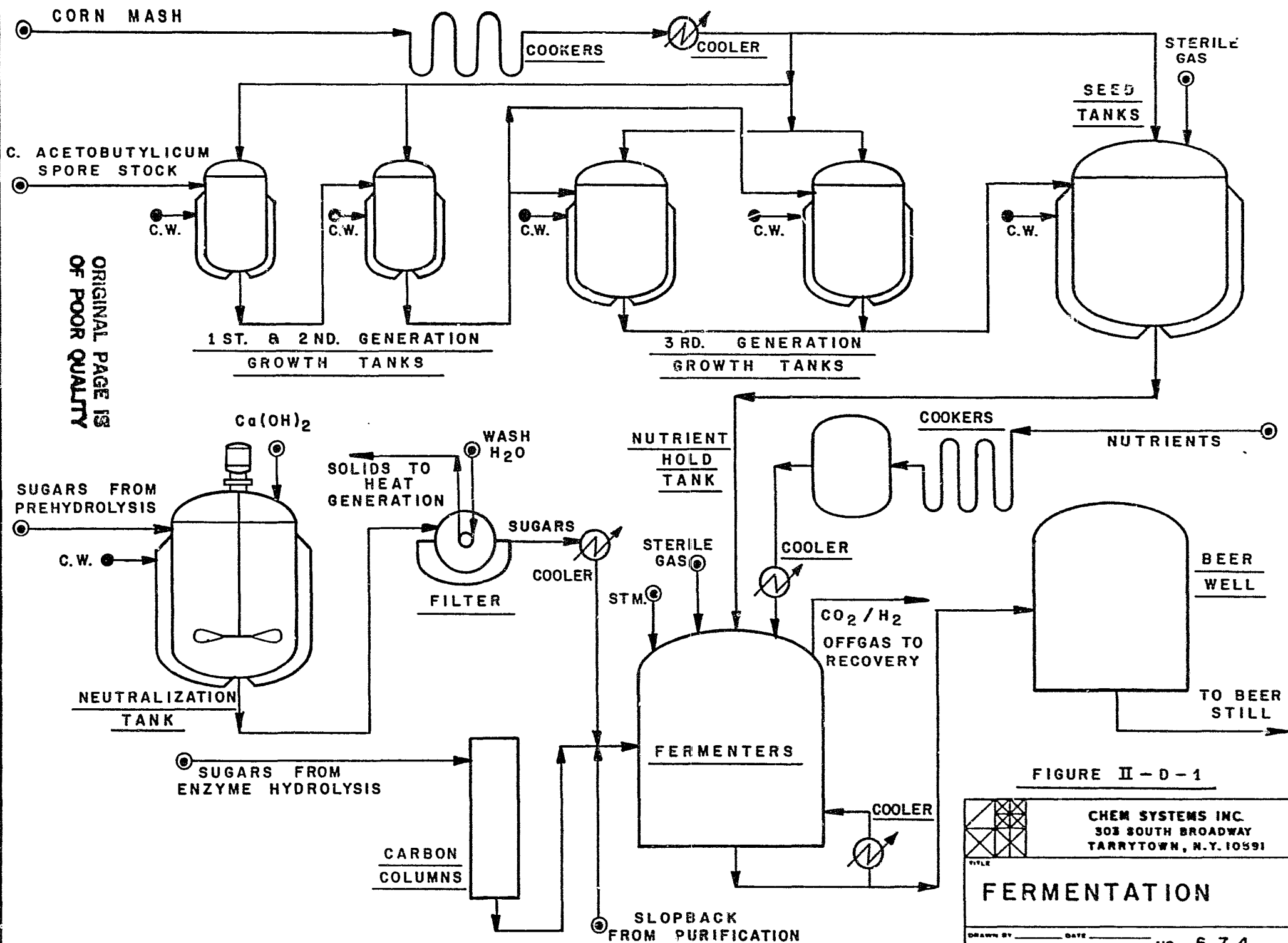


FIGURE II - D - 1

		CHEM SYSTEMS INC. 303 SOUTH BROADWAY TARRYTOWN, N.Y. 10591	
FERMENTATION			
DRAWN BY _____ APPROVED BY _____	DATE _____ DATE _____	NO 6 7 4	

evolved during fermentation is removed by a recirculation line and cooler on each tank. CO_2 and H_2 evolved during fermentation is vented from the tanks and sent to the CO_2 recovery system. Following fermentation, the beer is sent to a beer well prior to purification. The fermentation vessel is then washed free of residue, sterilized 4-5 hours with steam at 15 psig and cooled using sterile fermenter gas at 10-15 psig. It is then ready for the next fermentation cycle.

E. Purification

Figure III-E-1 provides the flow diagram for the purification section.

The fermentation beer is pumped from the beer well to a continuous beer still in the purification section. The dilute beer feed is first preheated against the stillage bottoms prior to entry into the column. The stillage is then split into two streams, one being recycled back to the fermenters, the other purged to the waste pond. Because of the extremely low concentration of the stillage stream, it is assumed that it will not be cost effective to recover a dried distillers grain type material as a byproduct in this scheme. The beer still produces a mixed 50 weight percent mixed solvent overhead which is condensed and sent to the beer storage tank. The majority of the steam consumed in the plant is required in the beer still because of the dilute beer feed.

The mixed solvent stream is sent to a batch column where the butanol, ethanol and acetone are fractionated in three streams. The acetone fraction is taken off the top of the column and sent to an acetone column where purified acetone is the overheads. The bottoms from the acetone column, containing a small fraction of mixed solvents, is recycled to the beer still feed. The ethanol-water azeotrope is the middle fraction from the batch column and is sent to storage. The third fraction is an 85 percent butanol water stream which is sent to the butanol column, where purified butanol is recovered as the bottoms and sent to storage. The overheads of the butanol column is a 70 percent butanol-water stream, which is decanted, and the organic layer (80 percent butanol) refluxed back to the column. The 4 percent butanol aqueous layer is recycled back to the beer still feed.

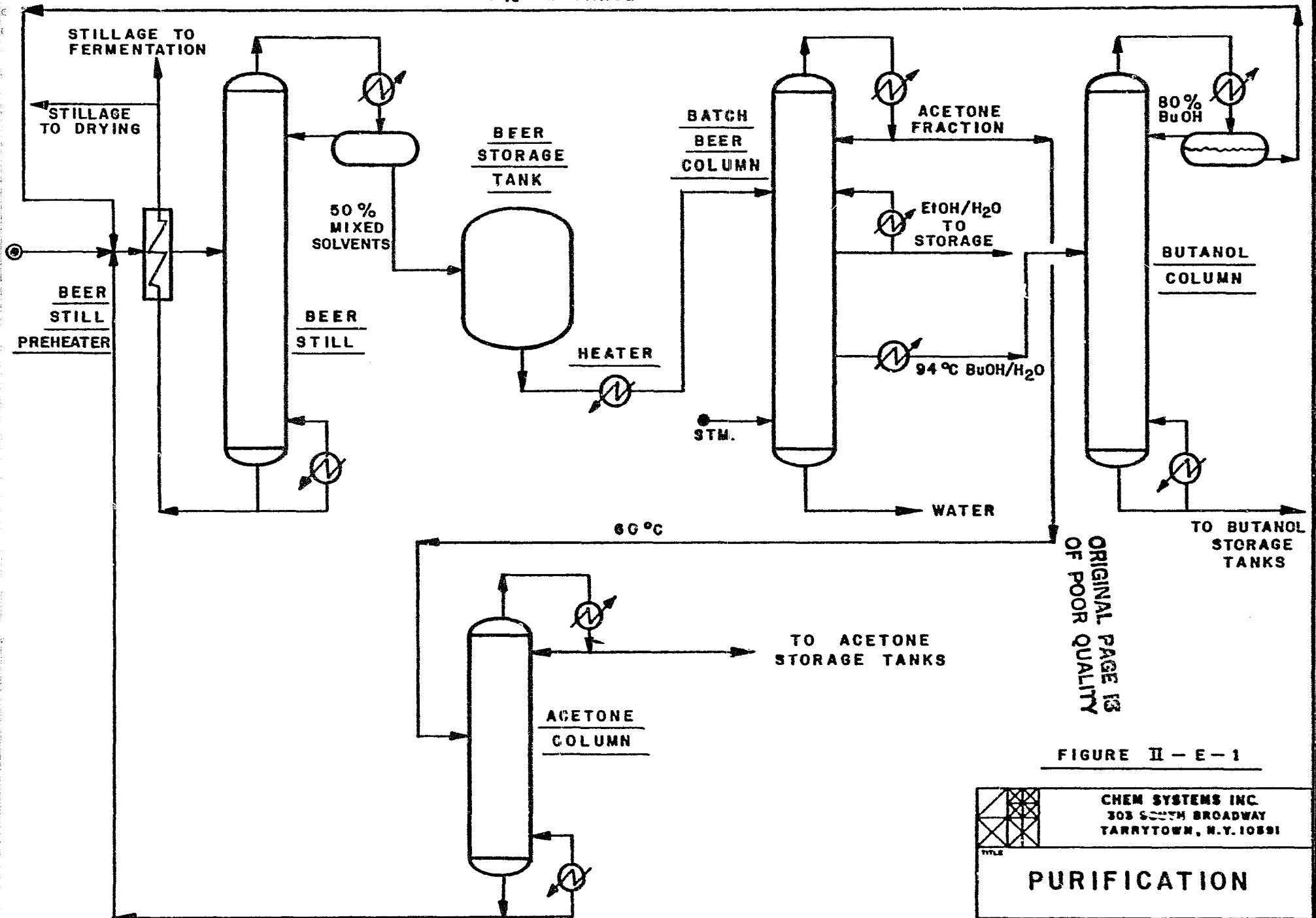
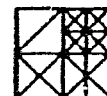


FIGURE II - E - 1



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F. Carbon Dioxide Recovery

Figure II-F-1 provides a flow diagram for the carbon dioxide recovery section.

When sugars are fermented to ethanol, large quantities of carbon dioxide are produced as a by-product of cell respiration. As the fermenters are usually closed vessels, it is possible to collect the off-gas and recover liquefied carbon dioxide for sale.

The carbon dioxide generated in the fermentation vessels passes through a foam trap to a low-pressure-drop water scrubber, where soluble impurities are removed. The scrubbed gas is then compressed to 300 psig in a nonlubricated, reciprocating compressor. Depending on the design pressure of the fermenters, it may be necessary to boost off-gas pressure prior to water washing, using a rotary positive displacement compressor.

The compressed gas is deodorized in a twin-tower, activated-carbon absorption system to remove remaining impurities. The carbon beds are periodically regenerated using live steam or hot air. The purified gas is then chilled and dried in a conventional alumina bed system to a dew point of -76°F .

The dry gas passes to a low-temperature stripper-condenser system, where the carbon dioxide is liquefied and separated from the non-condensable gases, mainly oxygen, which are vented to the atmosphere. The pure liquid carbon dioxide from the base of the stripper-condenser is then subcooled and sent to storage, where it is maintained under a pressure of about 300 psig.

G. Heat Generation

The filter bottoms from enzyme hydrolysis and fermentation are preheated with hot exhaust gases from the lignin boiler to 212°F prior to evaporation. A multiple-effect evaporator concentrates the lignin slurry to 50 weight percent solids prior to entry as fuel to the lignin fired boiler.

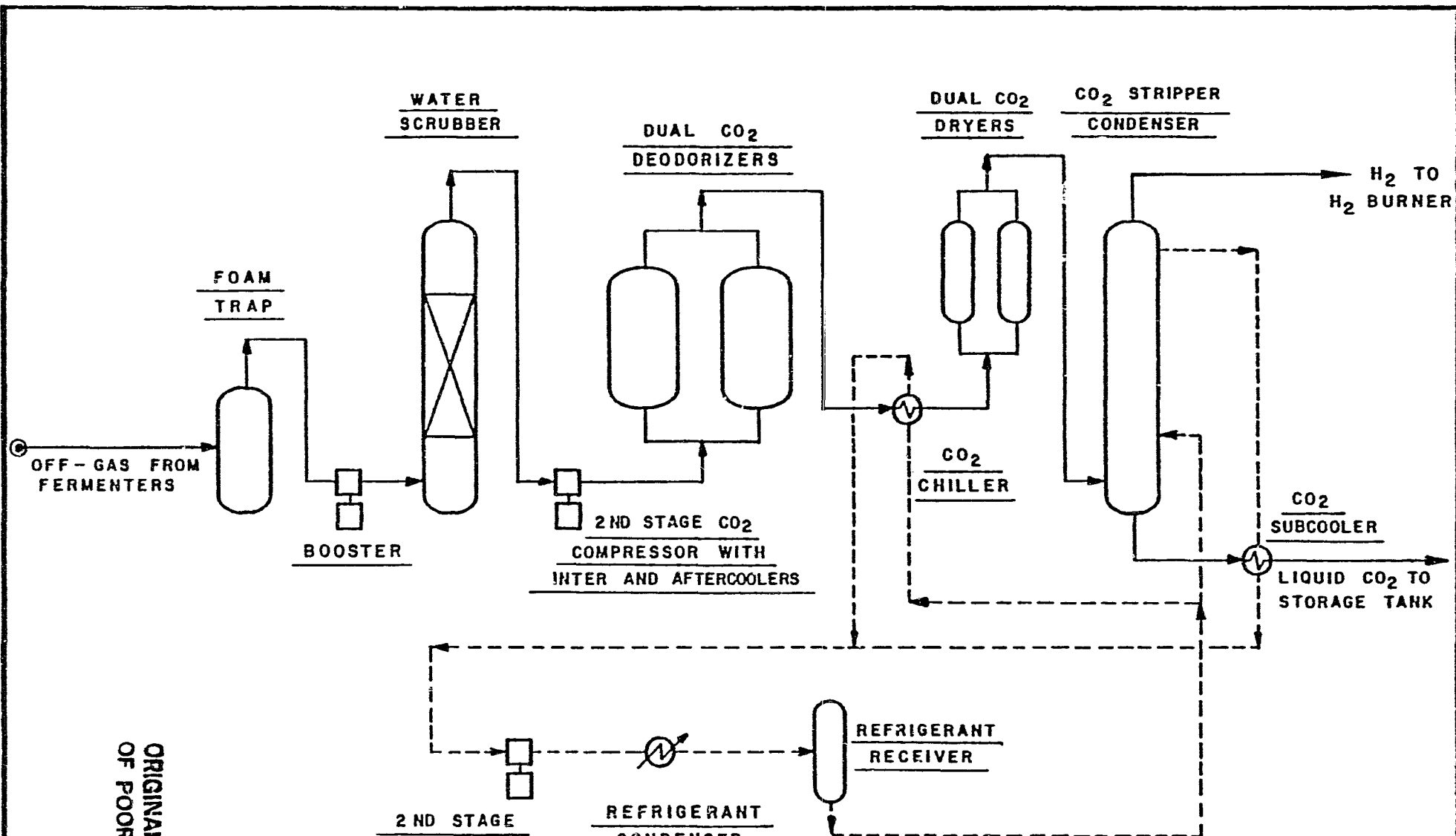


FIGURE II - F - 1

	CHEM SYSTEMS INC 303 SOUTH BROADWAY TARRYTOWN, N.Y. 10591	
	CARBON DIOXIDE RECOVERY	
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III ECONOMICS

A. Overall Process Economics

The cost of production (COP) estimate for butanol, acetone and ethanol produced via fermentation of wood hydrolyzates are provided in Tables III-A-1 and III-A-2 for the two cases analyzed. Table III-A-1 is the maximum yield case, and Table III-A-2 is the lower yield case. These data are summarized in Table III-A-3. Both cases produce 50 million gallons per year of mixed solvents at a plant located on the U.S. Gulf Coast in mid-1982. Table III-A-4 gives an ISBL capital breakdown for both cases.

Tables III-A-1 and III-A-2 indicate that the maximum yield case (3 percent sugar solution, 32 percent total yield, 1 percent solvents) produces mixed solvents at \$2.83 per gallon, while the lower yield case (5 percent sugar, 27.5 percent yield, 1.5 percent solvents) produces mixed solvents at \$2.58 per gallon. Both these values are the sales price of mixed solvents at 10 percent DCF. As can be seen from Table III-A-3, the major savings in COP for the low yield case is in a reduction of utilities cost, followed by a reduction in capital related expenses (overhead and DCF) of 12 cents per gallon. These two savings more than compensate for the maximum yield cases savings of 5 cents per gallon on raw material costs.

The cost of steam production and capital for steam production equipment is the most sensitive factor in the cost of production of mixed solvents via ABE fermentation. The savings in steam production cost associated with lower steam consumption, a smaller coal fired boiler and smaller equipment downstream of enzyme hydrolysis more than compensates for the raw material savings of the maximum yield case. Greater savings could probably be achieved in going to higher sugar concentrations, however, there are technical limits to these concentrations. Even if it is assumed that a microorganism can be developed which can tolerate butanol concentrations in excess of 1.3 percent, the maximum sugar concentration

TABLE III-A-1

COST OF PRODUCTION ESTIMATE FOR BUTANOL/ACETONE
PROCESS- FERMENTATIONORIGINAL PAGE IS
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CAPITAL SUMMARY

BASIS	CAPITAL COST	\$MILLION
Location: U.S. Gulf Coast	Battery Limits	96.1
Mid-1982	Offsites	110.4
Capacity: 50.0 million gallons/yr		
Str. Time: 8000 hours per year	Total Fixed Inv.	206.5
	Working Capital	23.0

PRODUCTION COST SUMMARY

RAW MATERIALS	UNITS PER GAL	PRICE, ¢/UNIT	ANNUAL COST, \$M	CENTS PER GAL
Aspen, lb	54.58436	1.0	27,280	
Sulfuric Acid, lb	.24511	4.3	527	
Calcium Hydroxide, lb	.17768	2.0	178	
Sodium Hydroxide, lb	.00784	26.0	102	
Corn, lb	.01238	4.5	28	
Sodium Sulfate, lb	.36476	3.0	547	
Superphosphate(46%), lb	1.58571	8.0	6,340	
Calcium Carbonate, lb	.72963	2.7	985	
Catalyst & Chemicals			1,900	
TOTAL RAW MATERIALS			37,886	75.80
UTILITIES				
Power, kWh	2.05092	4.6	4,715	
Cooling Water, M Gal	.32314	7.3	1,179	
Process Water, M Gal	.03021	65.0	981	
Steam, 50 psig, M Lb	.10625	470.0	24,957	
Steam, 200 psig, M Lb	.01141	480.0	2,736	
TOTAL UTILITIES			34,568	69.17
OPERATING COSTS				
Labor, 46 Men @ \$ 26,000	10 M/S		1,196	
Foremen, 9 Men @ \$ 29,600	1 M/S		266	
Supervision, 3 Man @ \$ 35,600	3 Man		107	
Maint., Material & Labor	6% of ISBL		5,766	
TOTAL OPERATING COST			7,335	14.68
OVERHEAD EXPENSES				
Direct Overhead	45% Lab. & Sup.		706	
Gen. Plant Overhead	65% Oper. Costs		4,768	
Insurance, Prop. Tax	1.5% Tot. Fix. Inv.		3,097	
Depreciation	20% ISBL + 10% OSBL		30,260	
TOTAL OVERHEAD EXPENSES			38,832	77.70
TOTAL COST OF PRODUCTION			118,621	237.35
BY-PRODUCT CREDIT				
Carbon Dioxide, lb	7.76847	2.8	10,871	
SCP, lb	.03461	15.0	259	
TOTAL BY-PRODUCT CREDIT			11,130	22.27
NET COST OF PRODUCTION			107,490	215.08
SALES PRICE AT 10% DCF				282.6

TABLE III-A-2

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PROCESS- FERMENTATIONCAPITAL SUMMARY

BASIS	CAPITAL COST	\$MILLION
Location: U.S. Gulf Coast	Battery Limits	92.8
Mid-1982	Offsites	97.3
Capacity: 50.0 million gallons/yr		-----
Str. Time: 8000 hours per year	Total Fixed Inv.	190.1
	Working Capital	21.2

PRODUCTION COST SUMMARY

	UNITS PER GAL	PRICE, ¢/UNIT	ANNUAL COST, \$M	CENTS PER GAL
<u>RAW MATERIALS</u>				
Aspen, lb	55.49477	1.0	27,735	
Sulfuric Acid, lb	.27792	4.3	597	
Calcium Hydroxide, lb	.19799	2.0	198	
Sodium Hydroxide, lb	.00880	26.0	114	
Corn, lb	.00850	4.5	19	
Sodium Sulfate, lb	.44020	3.0	660	
Superphosphate(46%), lb	1.91385	8.0	7,652	
Calcium Carbonate, lb	.88039	2.7	1,188	
Catalyst & Chemicals			1,950	

TOTAL RAW MATERIALS			40,114	80.26
<u>UTILITIES</u>				
Power, kWh	1.78079	4.6	4,094	
Cooling Water, M Gal	.30314	7.3	1,106	
Process Water, M Gal	.03301	65.0	1,072	
Steam, 50 psig, M Lb	.07363	470.0	17,296	
Steam, 200 psig, M Lb	.01298	480.0	3,113	

TOTAL UTILITIES			26,681	53.39
<u>OPERATING COSTS</u>				
Labor, 46 Men @ \$ 26,000	10 M/S		1,196	
Foremen, 9 Men @ \$ 29,600	1 M/S		266	
Supervision, 3 Man @ \$ 35,600	3 Man		107	
Maint., Material & Labor	6% of ISBL		5,568	

TOTAL OPERATING COST			7,137	14.28
<u>OVERHEAD EXPENSES</u>				
Direct Overhead	45% Lab. & Sup.		706	
Gen. Plant Overhead	65% Oper. Costs		4,639	
Insurance, Prop. Tax	1.5% Tot. Fix. Inv.		2,851	
Depreciation	20% ISBL + 10% OSBL		28,290	

TOTAL OVERHEAD EXPENSES			36,487	73.01
			=====	=====
TOTAL COST OF PRODUCTION			110,419	220.94
<u>BY-PRODUCT CREDIT</u>				
Carbon Dioxide, lb	8.12363	2.8	11,368	
SCP, lb	.03051	15.0	229	

TOTAL BY-PRODUCT CREDIT			11,597	23.20
			=====	=====
NET COST OF PRODUCTION			98,822	197.73
SALES PRICE AT 10% ICF				258.0

TABLE III-A-3SUMMARY OF ABE FERMENTATION PROCESS ECONOMICS

BASIS: 50 MM gals/yr, U.S. Gulf Coast, Mid-1982

	<u>Maximum Yield</u>	<u>Lower Yield</u>
Investment, \$MM		
Battery limits	96.1	92.8
Offsites	110.4	97.3
Total fixed investment	<u>206.5</u>	<u>190.1</u>
Cost of production, ¢/gal		
Raw materials	75.80	80.26
Utilities	69.17	53.39
Operating costs	14.68	14.28
Overhead expenses	77.70	73.01
Total cost of production	<u>237.35</u>	<u>220.94</u>
By-product credit	(22.27)	(23.20)
Net cost of production	<u>215.08</u>	<u>197.73</u>
Selling price at 10% DCF	282.6	258.0

TABLE III-A-4ISBL INVESTMENT BREAKDOWN FOR ABE FERMENTATION

MM\$

<u>Section</u>	<u>Maximum Yield</u>	<u>Lower Yield</u>
Prehydrolysis	25.4	28.8
Enzyme production	2.8	3.2
Enzyme hydrolysis	8.3	9.2
Fermentation	18.5	10.6
Purification	7.1	6.8
CO ₂ recovery	8.9	9.1
Heat generation	<u>4.1</u>	<u>4.5</u>
Total facility	75.1	72.2
Overhead	11.0	10.8
Contingencies	<u>10.0</u>	<u>9.8</u>
Total installed cost	96.1	92.8

currently obtainable from enzyme hydrolysis of wood is only 8 percent (assuming a maximum of 8 percent solids and delignified cellulose in the enzyme hydrolyzers). Therefore current technical feasibility would place an upper limit on sugar concentrations. However, it is apparent that the maximum sugar concentration compatible with current ABE technology, namely 6 percent, would offer the best economics for producing solvents via ABE fermentation of wood hydrozylates.

B. Discussion

An important objective of this assignment is to identify the most significant process elements in the overall production route, using two criteria: percentage of total production cost and percentage of energy consumption. The intent is to disaggregate the total cost of production and total energy consumption into three specific process blocks which can be labeled enzyme hydrolysis, fermentation and purification.

One difficulty which immediately arises in segregating cost of production by process element relates to allocation of raw material costs. Since the three process blocks are sequential, and a single raw material is charged in at the beginning of the sequence, a variety of arbitrary allocation methods can be postulated. Rather than bias the analysis with arbitrary assumptions, the approach taken herein is to present disaggregated cost of production economics on an ex-raw materials basis. In this way, the relative significance of capital costs and variable costs (utilities, operating costs and overheads) can be assessed for each of the three process blocks.

Table III-B-1 (A, B and C) indicates the specific production costs for each of the three process blocks (enzyme hydrolysis, fermentation, purification) for the maximum yield case. These are presented purely on a production cost basis (i.e., with no return). Similarly, Table III-B-2 (A, B and C) illustrates parallel data for the lower yield case. Both of these tables are summarized in Table III-B-3, which also compares the

TABLE III-B-1 (A)

Production Cost For Enzyme Hydrolysis (Maximum Yield)

Basis: 50 MM gals/year Solvents

ex. raw materials

			<u>Capital Cost</u> <u>\$ Million</u> ISBL 54.9 OSBL 32.8 Total 87.7	
	<u>UNITS/GAL</u>	<u>¢/UNIT</u>	<u>ANNUAL COST</u>	<u>¢/GAL</u>
<u>UTILITIES</u>				
Power, kwh	.6813	4.6	1567	
Cooling Water, M Gal	.0621	7.3	227	
Process Water, M Gal	.0294	65.0	956	
Steam, 50 psig, M lb	(.02688)	470.0	(6316)	
200 psig, M lb	.017824	480.0	4278	
<u>Total Utilities</u>			<u>712</u>	1.42
<u>OPERATING COSTS</u>				
	<u>TOTAL MEN</u>	<u>\$/MAN-YEAR</u>		
Labor	20	26,000	520	
Foremen	4	29,600	118	
Supervision	1	35,600	36	
Maint., Mat'l & Labor, 6% ISBL			3294	
<u>Total Operating Costs</u>			<u>3968</u>	7.94
<u>OVERHEAD EXPENSES</u>				
Direct Overhead	45% (Labor & Supervision)		303	
General Plant Overhead	65% Total Operating Cost		2579	
Insurance, Property Taxes	1.5% Total Fixed Investment		1316	
Depreciation	20% ISBL + 10% OSBL		14,260	
<u>Total Overhead Expenses</u>			<u>18,458</u>	36.92
Total				46.28

TABLE III-B-1 (B)

Production Cost For Fermentation (Maximum Yield) (Includes CO₂ Recovery)
 Basis: 50 MM gals/year Solvents
 ex. raw materials

			<u>Capital Cost</u> <u>\$ Million</u> ISBL 31.9 OSBL 10.0 Total 41.9	
	<u>UNITS/GAL</u>	<u>¢/UNIT</u>	<u>ANNUAL COST</u>	<u>¢/GAL</u>
<u>UTILITIES</u>				
Power, kwh	1.3518	4.6	3109	
Cooling Water, M Gal	.0434	7.3	158	
Process Water, M Gal	.00077	65.0	25	
Steam, 50 psig, M lb	-			
200 psig, M lb	(.00963)	480.0	(2311)	
<u>Total Utilities</u>			<u>981</u>	1.96
<u>OPERATING COSTS</u>				
	<u>TOTAL MEN</u>	<u>\$/MAN-YEAR</u>		
Labor	9	26,000	234	
Foremen	2	29,600	59	
Supervision	1	35,600	36	
Maint., Mat'l & Labor, 6% ISBL			1914	
<u>Total Operating Costs</u>			<u>2243</u>	4.49
<u>OVERHEAD EXPENSES</u>				
Direct Overhead	45% (Labor & Supervision)		148	
General Plant Overhead	65% Total Operating Cost		1458	
Insurance, Property Taxes	1.5% Total Fixed Investment		629	
Depreciation	20% ISBL + 10% OSBL		7380	
<u>Total Overhead Expenses</u>			<u>9615</u>	19.23
Total				25.68

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TABLE III-B-1 (C)

Production Cost For Purification (Maximum Yield)

Basis: 50 MM gals/year Solvents

ex. raw materials

			<u>Capital Cost</u> <u>\$ Million</u> ISBL 9.3 OSBL 67.6 Total 76.9	
	<u>UNITS/GAL</u>	<u>¢/UNIT</u>	<u>ANNUAL COST</u>	<u>¢/GAL</u>
<u>UTILITIES</u>				
Power, kwh	.0179	4.6	41	
Cooling Water, M Gal	.2176	7.3	794	
Process Water, M Gal	-	-	-	
Steam, 50 psig, M lb	.13313	470.0	31,285	
200 psig, M lb	.00322	480.0	773	
<u>Total Utilities</u>			<u>32,893</u>	65.79
<u>OPERATING COSTS</u>				
	<u>TOTAL MEN</u>	<u>\$/MAN-YEAR</u>		
Labor	17	26,000	442	
Foremen	3	29,600	81	
Supervision	1	35,600	36	
Maint., Mat'l & Labor, 6% ISBL			558	
<u>Total Operating Costs</u>			<u>1117</u>	2.23
<u>OVERHEAD EXPENSES</u>				
Direct Overhead	45% (Labor & Supervision)		251	
General Plant Overhead	65% Total Operating Cost		726	
Insurance, Property Taxes	1.5% Total Fixed Investment		1154	
Depreciation	20% ISBL + 10% OSBL		8620	
<u>Total Overhead Expenses</u>			<u>10,751</u>	21.50
<u>Total</u>				89.52

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TABLE III-B-2 (A)

Production Cost For Enzyme Hydrolysis (Lower Yield)

Basis: 50 MM gals/year Solvents

ex. raw materials

				<u>Capital Cost</u>	
				<u>\$ Million</u>	
				ISBL	61.6
				OSBL	37.7
				Total	99.3
	<u>UNITS/GAL</u>	<u>¢/UNIT</u>	<u>ANNUAL COST</u>		<u>¢/GAL</u>
<u>UTILITIES</u>					
Power,kwh	.7708	4.6	1773		
Cooling Water, M Gal	.0653	7.3	238		
Process Water, M Gal	.03244	65.0	1054		
Steam, 50 psig, M lb	(.0305)	470.0	(7167)		
200 psig, M lb	.02027	480.0	4864		
<u>Total Utilities</u>			<u>763</u>		1.53
<u>OPERATING COSTS</u>					
	<u>TOTAL MEN</u>	<u>\$/MAN-YEAR</u>			
Labor	24	26,000	624		
Foremen	5	29,600	135		
Supervision	1	35,600	36		
Maint., Mat'l & Labor, 6% ISBL			3696		
<u>Total Operating Costs</u>			<u>4491</u>		8.98
<u>OVERHEAD EXPENSES</u>					
Direct Overhead	45% (Labor & Supervision)		358		
General Plant Overhead	65% Total Operating Cost		2919		
Insurance, Property Taxes	1.5% Total Fixed Investment		1490		
Depreciation	20% ISBL + 10% OSBL		16,090		
<u>Total Overhead Expenses</u>			<u>20,857</u>		41.71
Total					52.22

TABLE III-B-2 (B)Production Cost For Fermentation (Lower Yield) (Includes CO₂ Recovery)

Basis: 50 MM gals/year Solvents

ex. raw materials

			<u>Capital Cost</u> <u>\$ Million</u> ISBL 22.7 OSBL 7.5 Total 40.2	
	<u>UNITS/GAL</u>	<u>¢/UNIT</u>	<u>ANNUAL COST</u>	<u>¢/GAL</u>
<u>UTILITIES</u>				
Power, kwh	.992	4.6	2282	
Cooling Water, M Gal	.0199	7.3	73	
Process Water, M Gal	.00057	65.0	19	
Steam, 50 psig, M lb	-	-	-	
200 psig, M lb	(.01052)	480.0	(2524)	
<u>Total Utilities</u>			<u>(150)</u>	(0.30)
<u>OPERATING COSTS</u>				
	<u>TOTAL MEN</u>	<u>\$/MAN-YEAR</u>		
Labor	10	26,000	260	
Foremen	2	29,600	59	
Supervision	1	35,600	36	
Maint., Mat'l & Labor, 6% ISBL			1362	
<u>Total Operating Costs</u>			<u>1717</u>	3.43
<u>OVERHEAD EXPENSES</u>				
Direct Overhead	45% (Labor & Supervision)		160	
General Plant Overhead	65% Total Operating Cost		1116	
Insurance, Property Taxes	1.5% Total Fixed Investment		603	
Depreciation	20% ISBL + 10% OSBL		5290	
<u>Total Overhead Expenses</u>			<u>7169</u>	14.34
<u>Total</u>				17.47

TABLE III-B-2 (C)

Production Cost For Purification (Lower Yield)
 Basis: 50 MM gals/year Solvents
 ex. raw materials

			<u>Capital Cost</u> <u>\$ Million</u>	
			ISBL 8.5	
			OSBL 52.1	
			Total 60.6	
	<u>UNITS/GAL</u>	<u>¢/UNIT</u>	<u>ANNUAL COST</u>	<u>¢/GAL</u>
<u>UTILITIES</u>				
Power, kwh	.0172	4.6	40	
Cooling Water, M Gal	.21794	7.3	795	
Process Water, M Gal	-	-	-	
Steam, 50 psig, M lb	.10413	470.0	24,471	
200 psig, M lb	.00323	480.0	775	
<u>Total Utilities</u>			<u>26,081</u>	52.16
<u>OPERATING COSTS</u>	<u>TOTAL MEN</u>	<u>\$/MAN-YEAR</u>		
Labor	12	26,000	312	
Foremen	2	29,600	59	
Supervision	1	35,600	36	
Maint., Mat'l & Labor, 6% ISBL			510	
<u>Total Operating Costs</u>			<u>917</u>	1.83
<u>OVERHEAD EXPENSES</u>				
Direct Overhead	45% (Labor & Supervision)		183	
General Plant Overhead	65% Total Operating Cost		596	
Insurance, Property Taxes	1.5% Total Fixed Investment		909	
Depreciation	20% ISBL + 10% OSBL		6900	
<u>Total Overhead Expenses</u>			<u>8588</u>	17.18
<u>Total</u>				71.17

TABLE III-B-3

Utility, Operating and Overhead Expenses by Plant
Section as a Percent of Total Cost of Production

<u>Section</u>	<u>Maximum Yield Case - Total COP - 215.08 ¢/gal</u>			<u>Section Total</u>	<u>% Total COP</u>
	<u>COP ¢/gal</u>	<u>Utilities</u>	<u>Operating</u>		
Enzyme Hydrolysis	1.42	7.94	36.92	46.28	21.5
Fermentation	1.96	4.49	19.23	25.68	12.0
Purification	65.79	2.23	21.50	89.52	41.6
Raw Materials (minus by-product credit)				53.53	24.9

<u>Lower Yield Case - Total COP - 197.73 ¢/gal</u>					
Enzyme Hydrolysis	1.53	8.98	41.71	52.22	26.4
Fermentation	(.3)	3.43	14.34	17.47	8.8
Purification	52.16	1.83	17.18	71.17	36.0
Raw Materials (minus by-product credit)				57.06	28.9

significance of individual cost items by plant section as a percent of total cost of production. For completeness, the percentage of production costs represented by raw materials (less by-product credits) is also indicated, since these costs were not allocated by process element. It is apparent from this table that the largest single item is the cost of utilities in the purification section. Certainly in the maximum yield case, the cost of utilities for purification is larger than the total cost (utilities + operating + overhead) for either of the other two sections. In the lower yield case, the cost of utilities for purification remains the largest cost item although overhead costs in the enzyme hydrolysis section (primarily associated with depreciating capital equipment) become more significant. Thus, there is a trade off: as one goes to lower yields, the utilities required for purification are reduced but are offset to some extent by increased capital costs required in the enzyme hydrolysis section.

Table III-B-4 provides detail on the steam consumption by plant section. Subsections are grouped into the three process blocks previously indicated, so that the enzyme hydrolysis section is broken down into four subsections (prehydrolysis, enzyme production, enzyme hydrolysis, heat generation) and the fermentation section is broken down into two subsections (fermentation and carbon dioxide recovery). Values indicated as steam consumption actually represent fuel consumed to generate steam, assuming a steam generation efficiency of 85 percent. In cases where credits are shown, these also reflect an 85 percent efficiency since the energy recovered offsets equivalent fuel which would be used to generate steam.

The data in Table III-B-4 are combined with electric energy consumption data (converted to Btus using a heat rate of 10,000 Btus per kwh) in Table III-B-5. This table presents the relative significance of total energy consumption by plant section. As indicated, the purification section is overwhelmingly the largest energy consumer. By virtue of the heat generated in the enzyme hydrolysis section, this section is

TABLE III-B-4

Steam Consumption by Plant Section

	<u>Maximum Yield Case Steam MMBtu/yr</u>	<u>Lower Yield Case Steam MMBtu/yr</u>
Prehydrolysis	885,448	1,004,459
Enzyme Production	-	-
Enzyme Hydrolysis	-	-
Heat Generation	(1,461,007)	(1,657,286)
Fermentation	34,870	15,948
CO ₂ Recovery	(513,504)	(537,140)
Purification	<u>7,236,446</u>	<u>5,658,698</u>
Total	6,182,253	4,484,679

TABLE III-B-5

Total Energy Consumption by Plant Section
MMBtu/yr

Maximum Yield Case

<u>Section</u>	<u>Steam</u>	<u>Power</u>	<u>Section Total</u>	<u>% Total</u>
Enzyme Hydrolysis	(575,559)	340,650	(234,909)	-3.26
Fermentation	(478,634)	675,900	197,266	2.74
Purification	<u>7,236,446</u>	<u>8,950</u>	<u>7,245,396</u>	<u>100.52</u>
Total	6,182,253	1,025,500	7,207,753	100.00

Lower Yield Case

Enzyme Hydrolysis	(552,827)	385,400	(267,427)	-4.98
Fermentation	(521,192)	496,000	(25,192)	-.47
Purification	<u>5,659,698</u>	<u>8,600</u>	<u>5,667,298</u>	<u>105.45</u>
Total	4,484,679	890,000	5,374,679	100.00

indicated to be a net energy producer. In actuality, the energy produced would be more than offset by an allocation of the energy represented by raw materials. As previously indicated, such an allocation has not been performed. Nonetheless, the relative significance of the three process blocks is clear.

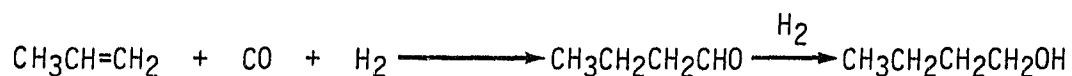
It is apparent from the foregoing discussion that the purification step is the most significant plant section relative to total cost of production and specifically to energy consumption. This is due primarily to the steam required to concentrate the very dilute beer obtained in ABE fermentation. It follows, therefore, that future research and development efforts might well concentrate on reducing the steam consumption of the purification step. This can be accomplished via two different approaches:

1. reduce energy consumption of the purification step by improved separation techniques such as reverse osmosis, membrane separation, solvent extraction, adsorption, etc.
2. develop a microorganism via genetic manipulation which has the ability to ferment wood sugars with satisfactory yields and can tolerate higher butanol concentrations (greater than 1.3 percent) than presently used microorganisms.

Successful research in either approach, or even a combination of both, could significantly reduce the cost of producing solvents via ABE fermentation.

IV. CONVENTIONAL TECHNOLOGYA. ButanolChemistry

Butanol production is based on two technologies: cobalt-catalyzed or rhodium-catalyzed carbonylation of propylene. Both systems are currently utilized commercially, but the noble metal-based catalysts appear to have a slight advantage for new plants primarily because they allow lower operating pressures and afford higher yields of normal butanol. The carbonylation reactor initially forms butyraldehyde, which can be simultaneously or separately hydrogenated to n-butanol:



The hydroformylation reaction is homogeneously catalyzed and employs either cobalt carbonyl, rhodium carbonyl, phosphine-modified cobalt carbonyl or phosphine (or amine)-modified rhodium carbonyl as the active form of the catalyst. Although modified rhodium or cobalt catalysts allow lower pressures than unmodified catalysts, they require higher temperatures since they give rise to considerably slower reaction rates. All catalysts cause hydrogenation of the feed olefin to propane in varying degrees. The extent of in-situ hydrogenation of the aldehyde to alcohol in the carbonylation reactor also varies with catalyst type and reaction conditions, and can be varied from practically nil to almost 100 percent. When the hydrogenation reaction is performed separately, it can use Raney nickel, Raney copper, copper chromite, cobalt phosphine complexes or nickel on kieselguhr as the hydrogenation catalyst.

The process description for the rhodium phosphine-catalyzed process is reviewed below.


Process Description

A process flow diagram for the production of butanol via rhodium-based carbonylation is presented in Figure IV-A-1. Synthesis gas having a hydrogen to carbon monoxide molar ratio of 1.02 is supplied over-the-fence from a partial oxidation plant. It is first purified to remove trace impurities, chiefly sulfur, in two alternately fed packed-bed columns filled with zinc oxide. This gas, supplied at 750 psig, does not require additional compression for feeding into the aldehyde reactors. The level of sulfur fed to the reactors is maintained below 1 ppm to reduce poisoning of the rhodium catalyst.

Liquid propylene feed (94.5 weight percent propylene) passes through two alternately fed molecular sieve dryers, which guard against trace quantities of water and dienes entering the aldehyde reactors. Trace quantities of water, if not removed, require expensive materials of construction for the reactor system. The liquid propylene can either be injected directly into the aldehyde reactors or combined with recycle propylene/propane.

The active catalyst complex in the two reactors is $\text{HRh}(\text{CO})_2(\text{PO}_3)_2$, which is formed in the reactor itself by the reaction of the synthesis gas with a rhodium salt and triphenylphosphine. A very high ratio of ligand (triphenylphosphine) to active catalyst complex is required in the reactors to give a 10:1 ratio of normal to isoaldehyde in the reactor product, leading to a concentration in the reactors of several weight percent of triphenylphosphine. Triphenylphosphine ligand and rhodium make-up are blended in the blend tanks and go intermittently to the catalyst storage tanks, from where they pass to the reactors. A slipstream from the reactors helps to dissolve the catalyst make-up and also provides for occasionally drawing off spent catalyst to maintain activity in the reactors. Two full charges of rhodium catalysts are required for the plant: one is present in the reactor and the second is held for make-up in a safe storage area.



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The Oxo reaction system is dual-train, with a spare recycle gas compressor serving both trains. The main material in contact with the process fluids is 304 L stainless steel.

A 304 stainless steel turbine agitator is top-mounted on the reactors for catalyst agitation, particularly during start-up and during short shutdowns. The agitation avoids excessive coagulation of the catalyst and helps transfer heat to the cooling coils. The reactors have submerged cooling coils for partial removal of the heat of reaction. Liquid level is held at one half of the reactor volume, with enough disengagement space for the removal of entrained reactant liquids.

The crude vapor product, along with unreacted syngas and propylene, is taken overhead to the entrainment separators, from which traces of the catalyst are recycled to the aldehyde reactors by a gravity flow liquid trap. There is no downstream capability for catalyst recovery during normal operation because the catalyst remains in the reactor. The low conversion of the feed gases provides sufficient stripping volume so that all of the reaction products, including the heavy dimers, trimers, and diols, are stripped out of the reaction liquid. If polymer-grade propylene were to be used as feed, then a lower conversion would be necessary to ensure that enough gas is recycled to get adequate stripping; however, considerably less propylene would be lost in the purge stream.

Reactor temperature and pressure are controlled by regulating the cooling water flow to the exchanger that cools the recycle gases. A purge from the recycle stream maintains the concentration of recycled propane at a constant level.

The crude liquefied product mixture goes to the stripping column, from which the unreacted propylene plus recycle propane recycles to the reactor. Components of the ten-sieve tray stripping column system are made of carbon steel.

The bottoms from the stripping column are cooled to 60°C and combined with hydrogen that has been compressed (if necessary) to 150 psi; they enter the aldehyde hydrogenation reactor, which is packed with 40 weight percent nickel on kieselguhr.

The liquid hourly space velocity is 4 cubic feet of feed as liquid per cubic foot of catalyst per hour, and approximately 4 mols of hydrogen are used per mol of feed. Unconverted hydrogen is recompressed and recycled.

The hydrogenation product consists of dissolved gases, butanols, and water, which are separated in the butanol distillation section. The light ends column separates the dissolved gases and light ends and removes the water as overhead product for disposal. An organic waste layer separates in the reflux drum and goes to disposal. Like all the butanol distillation towers and equipment, the light ends column is made of carbon steel. The column has 94 trays and the condenser is air-cooled. Separation of the isobutanol and n-butanol from the bottom of the light ends column takes place in two columns. In the first, with 120 trays, isobutanol is taken overhead with a purity of 99.8 weight percent, and in the second, with 40 trays, the n-butanol also separates as the overhead product with a purity of 99.9 weight percent. The bottoms product is a heavies stream, which is withdrawn as a purge for disposal.

B. Acetone

Chemistry

A number of processes are available for the conversion of propylene to acetone.

- From propylene to isopropanol, followed by dehydrogenation to acetone.
- From propylene to isopropanol, followed by oxidation to acetone and hydrogen peroxide.
- By direct oxidation of propylene to acetone.

The best known of these involve isopropanol as an intermediate.

The first route is the most common at the present time and accounts for about one quarter of the world's acetone production. The first stage in the process is the production of isopropanol from propylene. The traditional route to isopropanol is by an indirect or esterification-hydrolysis process using sulphuric acid. Propylene is first absorbed in 75 percent sulphuric acid to form a solution of diisopropyl sulphate and isopropyl acid sulphate. The sulphated hydrocarbon solution is converted to an acid solution of isopropanol, ether and polymer by hydrolysis with dilution water. The hydrocarbons are separated from the acid, neutralized with caustic and fractionated to separate the three main components. Ether is recycled to the reactor and the ether-free isopropanol is distilled to yield an 87 percent isopropanol/water azeotrope. The overall reactions are as follows:



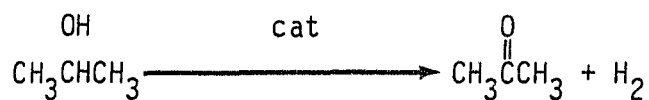
This route to isopropanol is still used in many plants. In the last few years, however, direct hydration processes have been developed, and these will probably be used in all future installations. Propylene and water are preheated and fed to a catalytic reactor, where isopropanol is formed.

The reaction may be carried out in the vapor or liquid phase at pressures of 25 to 250 bar and at temperatures of 150 to 300°C. Typical catalysts are supported phosphoric acid, cation exchange resins, manganese oxide, alumina, silica and molybdenum, tungsten oxide or nitride and solutions of polyanions containing tungsten atoms. Conversion per pass depends on the process used and is typically between 5 percent for vapor-phase reactions to 60-70 percent for liquid-phase reactions.

The reactor effluent, after heat exchange with the reactor feed, is sent to a water scrubber, where isopropanol is separated from unreacted propylene, which is then recycled to the reactor. Aqueous isopropanol is separated from water and small amounts of other light and heavy ends in a series of three to six distillation columns, depending upon whether anhydrous isopropanol is required as well as the 87 percent azeotrope. Benzene is often used as the azeotrope breaker. Process yields are about 93 to 97 percent of theoretical, based on the conversion of propylene to isopropanol. The overall chemical reaction is as follows:



The dehydrogenation of isopropanol is a simple reaction. It is vaporized and fed over a fixed bed catalyst in a tubular reactor, where endothermic dehydrogenation occurs. Typical operating conditions are 0.34 bar and 530-550°C. A brass or zinc oxide catalyst is commonly used. The process yield of acetone from isopropanol is above 95.5 percent, and conversion per pass through the reactor is over 90 percent. The endothermic heat of reaction is supplied by a circulating stream of flue gas heated by direct combustion. Catalyst performance drops gradually during operation because of fouling, and it must be regenerated approximately every ten days by burning off organic material with a mixture of 2 percent oxygen and 98 percent nitrogen at about 500°C. The overall chemical reaction is as follows:



The isopropanol used is usually the 87 percent azeotrope since water does not interfere with the reaction. The reactor effluent is scrubbed to clean up the hydrogen. Purification is carried out using conventional fractionation techniques, and unconverted isopropanol is recycled as the water azeotrope.

Process Description

A process for making acetone from propylene is described in this section. The process, shown diagrammatically in Figure IV-B-1, involves the direct hydration of propylene to isopropanol and the subsequent catalytic dehydrogenation of the isopropanol to acetone. The flow scheme is based generally on the Tokuyama Soda process for hydration and on the BP Chemicals process for dehydrogenation.

Propylene of at least 95 percent purity is preheated and fed to the hydration reactor with fresh water and aqueous recycle catalyst stream. The reaction between water and the dissolved propylene occurs in a liquid phase at 150-200 bar and 240 to 270°C to produce isopropanol.

The isopropanol product solution from the reactor is cooled by heat exchange with reactor feed water and then flashed under reduced pressure in a gas separator. Dissolved unreacted propylene is released and condensed for recycle to the reactor. The separated liquid is sent to the azeotrope column, where an azeotropic mixture of isopropanol and water is drawn off and sent to a second column for removal of light ends. The aqueous solution containing catalyst from the bottom of the azeotrope column joins the fresh water feed and is recycled to the reactor.

The 87 percent isopropanol azeotrope from the lights column is vaporized and fed to a multitubular reactor, where endothermic dehydrogenation takes place. The reactor tubes are filled with catalyst and are carried between steel tube plates mounted within an outer steel shell. Flue gases are circulated by a fan at high velocity in a direction normal to the axis of the tubes. The flue gases are heated by direct combustion, and excess gas is bled to the atmosphere. The circulation rate is such that the temperature of the flue gases does not drop by more than a few degrees during passage across the tubes. The temperature difference between the flue gases and the maximum temperature attained in the tubes is about 20°C.

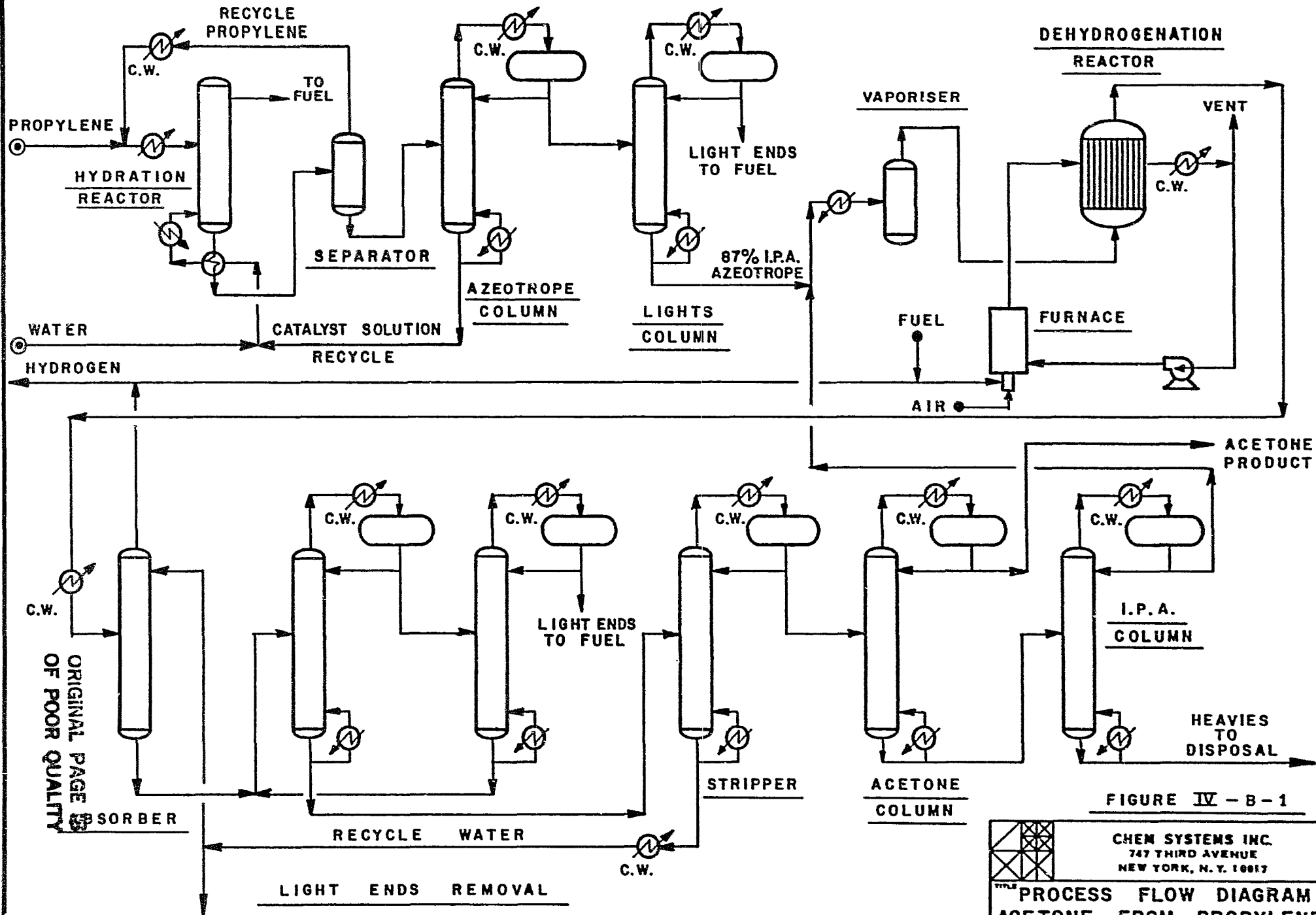
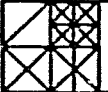


FIGURE IV - B - 1

 CHEM SYSTEMS INC. 747 THIRD AVENUE NEW YORK, N. Y. 10017	
PROCESS FLOW DIAGRAM ACETONE FROM PROPYLENE VIA I. P. A.	
DRAWN BY _____ APPROVED BY _____	DATE _____ DATE _____
NO. 674	

Vapors leaving the catalyst chamber are cooled, and about half the acetone present is condensed. The uncondensed hydrocarbons are washed out of the hydrogen stream by passage up a packed tower countercurrent to a flow of water. The hydrogen from the absorption tower can be used without additional purification in hydrogenation processes or it can be used as fuel for the reactor heating circuit, in which case the hydrogen output approximately balances fuel requirements.

Low-boiling impurities (mostly derived from impurities in the isopropanol) are removed from the crude acetone stream from the bottom of the absorber before it is fed to a stripping tower. Water from the base of the stripper is cooled and recycled to the absorber. The overhead mixture of acetone, isopropanol, water and a small amount of high-boiling impurities is further distilled to yield the pure acetone product, an isopropanol recycle stream (which is returned to the reactor), and a heavies stream (which goes for disposal).

C. Economics

The cost of production (COP) estimates for the conventional routes to butanol and acetone are provided in Tables IV-C-1 and IV-C-2 respectively. These data are summarized in Table IV-C-3. Both butanol and acetone facilities produce 50 million gallons per year of product at a plant located on the U.S. Gulf Coast in mid-1982.

Table IV-C-1 indicates that butanol can be produced at a net cost of production of approximately 2.00 dollars per gallon. The sales price of butanol at 10 percent DCF is 2.35 dollars per gallon. Table IV-C-2 indicates that acetone can be produced at a net cost of production of 1.96 dollars per gallon which translates to a selling price of 2.32 dollars per gallon at 10 percent DCF.

TABLE IV-C-1COST OF PRODUCTION ESTIMATE FOR ACETONE
PROCESS- IPA DEHYDROGENATIONCAPITAL SUMMARY

<u>BASIS</u>	<u>CAPITAL COST</u>	<u>\$MILLION</u>
Location: U.S. Gulf Coast	Battery Limits	41.2
Mid-1982	Offsites	29.2
Capacity: 50.0 million gallons/yr		-----
Str. Time: 8000 hours per year	Total Fixed Inv.	70.4
	Working Capital	15.3

PRODUCTION COST SUMMARY

<u>RAW MATERIALS</u>	<u>UNITS</u>	<u>PRICE,</u>	<u>ANNUAL</u>	<u>CENTS</u>
	<u>PER GAL</u>	<u>c/UNIT</u>	<u>COST, \$M</u>	<u>PER GAL</u>
Propylene(95%), lb	5.31926	25.0	66,450	
Catalyst & Chemicals			1,260	

TOTAL RAW MATERIALS			67,710	135.50
<u>UTILITIES</u>				
Power, kWh	.99511	4.6	2,287	
Cooling Water, M Gal	.29828	7.3	1,088	
Process Water, M Gal	.00060	65.0	20	
Steam, 200 psig, M Lb	.03968	480.0	9,518	

TOTAL UTILITIES			12,913	25.84
<u>OPERATING COSTS</u>				
Labor, 32 Men @ \$ 26,000		6 M/S	832	
Foremen, 7 Men @ \$ 29,600		1 M/S	207	
Supervision, 1 Man @ \$ 35,600		1 Man	36	
Maint., Material & Labor		6% of ISBL	2,472	

TOTAL OPERATING COST			3,547	7.10
<u>OVERHEAD EXPENSES</u>				
Direct Overhead	45% Lab. & Sup.		484	
Gen. Plant Overhead	65% Oper. Costs		2,305	
Insurance, Prop. Tax	1.5% Tot. Fix. Inv.		1,056	
Depreciation	20% ISBL + 10% OSBL		11,160	

TOTAL OVERHEAD EXPENSES			15,005	30.03
			=====	=====
TOTAL COST OF PRODUCTION			99,175	198.47
<u>BY-PRODUCT CREDIT</u>				
Propane, lb	.26596	8.8	-1,170	

TOTAL BY-PRODUCT CREDIT			-1,170	-2.34
			=====	=====
NET COST OF PRODUCTION			98,006	196.13
SALES PRICE AT 10% DCF				232.4

TABLE IV-C-2

ORIGINAL PAGE IS
OF POOR QUALITYCOST OF PRODUCTION ESTIMATE FOR BUTANOL
PROCESS- PROPYLENE CARBONYLATCAPITAL SUMMARY

BASIS	CAPITAL COST	\$MILLION
Location: U.S. Gulf Coast	Battery Limits	81.2
Mid-1982	Offsites	28.8
Capacity: 50.0 million gallons/yr		
Str. Time: 8000 hours per year	Total Fixed Inv.	90.0
	Working Capital	16.7

PRODUCTION COST SUMMARY

RAW MATERIALS	UNITS PER GAL	PRICE, ¢/UNIT	ANNUAL COST, \$M	CENTS PER GAL
Propylene(94.5%), lb	5.20319	25.0	65,000	
Synthesis Gas, MSCF	.08525	250.0	10,650	
Hydrogen, MSCF	.03792	300.0	5,685	
Catalyst & Chemicals			1,400	

TOTAL RAW MATERIALS			82,735	165.57
UTILITIES				
Power, kWh	.65410	4.6	1,504	
Cooling Water, M Gal	.05613	7.3	205	
Inert Gas, MSCF	.00135	123.0	83	
Fuel, MM BTU	.02772	346.0	4,792	
Steam, 600 psig, M Lb	.02161	538.0	5,810	

TOTAL UTILITIES			2,810	5.62
OPERATING COSTS				
Labor, 32 Men @ \$ 26,000	6 M/S		832	
Foremen, 7 Men @ \$ 29,600	1 M/S		207	
Supervision, 1 Man @ \$ 35,600	1 Man		36	
Maint., Material & Labor	6% of ISBL		3,672	

TOTAL OPERATING COST			4,747	9.50
OVERHEAD EXPENSES				
Direct Overhead	45% Lab. & Sup.		484	
Gen. Plant Overhead	65% Oper. Costs		3,095	
Insurance, Prop. Tax	1.5% Tot. Fix. Inv.		1,350	
Depreciation	20% ISBL + 10% OSBL		15,120	

TOTAL OVERHEAD EXPENSES			20,039	40.10
			=====	=====
TOTAL COST OF PRODUCTION			110,330	220.80
BY-PRODUCT CREDIT				
Isobutanol, lb	.74546	28.5	10,616	

TOTAL BY-PRODUCT CREDIT			10,616	21.25
			=====	=====
NET COST OF PRODUCTION			99,714	199.55
SALES PRICE AT 10% DCF				235.1

TABLE IV-C-3

SUMMARY OF PROCESS ECONOMICS
FOR CONVENTIONAL ROUTES TO BUTANOL AND ACETONE
Basis: 50MM gals/yr, US Gulf Coast, mid-1982

	<u>Butanol</u>	<u>Acetone</u>
Investment, \$MM		
Battery limits	61.2	41.2
Offsites	28.8	29.2
Total fixed investment	90.0	70.4
Cost of production, ¢/gal		
Raw materials	165.57	135.5
Utilities	5.62	25.84
Operating costs	9.50	7.10
Overhead expenses	40.10	30.03
Total cost of production	220.80	198.47
By-product credit	(21.25)	(2.34)
Net cost of production	199.55	196.13
Selling price at 10% DCF	235.1	232.4

V. CONCLUSIONS AND RECOMMENDATIONS

A comparison of the process economics of the conventional routes to butanol-acetone versus the fermentation route indicates the conventional route holds an advantage of 20-25 cents per gallon or approximately 10 percent. This would indicate that although the fermentation route is still not competitive with the conventional routes to butanol-acetone, the gap is narrow and could disappear given potential research advances and process optimization in the near future.

It is also apparent that, with regard to the fermentation route, the most significant plant section relative to total dollar and energy cost is the purification step. This is due primarily to the steam required to concentrate the very dilute beer obtained in ABE fermentation. It follows, therefore, that future research and development efforts might well concentrate on reducing the steam consumption of the purification step, either through improved separation techniques or the development through genetic manipulation of a microorganism for fermentation which can tolerate higher butanol concentrations.

While this particular analysis was limited to a technical and economic evaluation of a specific butanol/acetone from wood process, a broader goal from the ECUT perspective would be to extend the work via parametric analysis in order to establish and rank R & D options. Using the methodology developed herein as a tool, a more generic analysis can be constructed which focuses initially on butanol/acetone fermentation and ultimately on a wider range of chemicals which can be produced via similar processing routes.

Candidate options for the parametric analysis are recommended below, by plant segment:

I. Feedstock

A. The effect on overall process economics of:

i) Varying feedstock prices.

- ii) Varying feedstocks. Some examples of feedstocks which might be considered are agricultural wastes, different wood species, municipal solid waste, whey and sulfite liquor.

II. Pretreatment and Enzyme Hydrolysis

- A. The effect on overall process economics of using steam explosion pretreatment, lignin extraction and/or enzyme recovery in addition to or in place of certain steps in the present scheme. Lignin extraction will probably be required following pretreatment if lignin is to be utilized as a higher value by-product (rather than its fuel value).
- B. Update enzyme production step to reflect recent advances in the production of a β -glucosidase- β -glucanase enzyme mix from different fungi.

III. Fermentation

- A. The effect on overall process economics of:
 - i) The relationship of initial sugar concentration, fermentation time and solvent yield for wood (xylose/glucose) sugar streams.
 - ii) Varying nutrient media and solvent ratio.
 - iii) Improvements in microorganism product tolerance and product yield via genetic manipulation.
 - iv) Continuous fermentation scheme versus conventional batch fermentation.

IV. Purification

A. The effect on overall process economics of utilizing alternate purification schemes presently under development. These could possible include:

- i) Solvent extraction
- ii) Membrane separation
- iii) Adsorption
- iv) Improved distillation
- v) Reverse osmosis

V. By-product Utilization

A. The technical feasibility and effect on overall process economics of utilizing lignin as a high value by-product. Possibilities include:

- i) A substitute petrochemical feedstock for the production of phenolic resins.
- ii) Recognizing that the structure of lignin contains only monoaromatics with hydroxy and methoxy groups attached to them, lignin could potentially be used as a raw material for producing such chemicals as phenol, benzene, cresols and catechols. One speculative route developed by HRI, for example, involves hydrocracking and hydrodealkylation of lignin to a mixture of phenol, benzene and fuel oil.

GLOSSARY

This glossary is intended to acquaint readers who are unfamiliar with production cost analysis with some of the terms used in this report.

Battery Limits

See Inside Battery Limits (ISBL) Investment

By-Product Credit

The value of by-products based on their unit market price.

Cost of Production, Net (COP)

The difference between Total Cost of Production and By-Product Credits

Cost of Production, Total (COP)

The cost per unit of product, accounting for variable costs such as raw materials, utilities, labor, fixed cost (including return on investment and overhead), depreciation, and other capital-related charges.

Direct Overhead

Payroll costs, in addition to wages and salaries, which are directly attributable to operating and supervisory personnel. These include items such as company payments to payroll taxes, medical plan, retirement fund, vacations and any other so-called "fringe" benefits.

General Plant Overhead

Expenses comprising the cost of servicing a given installation. These costs include items such as administrative expenses, plant security, fire protection, general area maintenance, and employees' cafeteria.

Inside Battery Limits (ISBL) Investment

The portion of total plant capital cost related to equipment for the production process. Examples of ISBL costs include reaction vessels, distillation columns and heat exchangers.

Offsites

See Outside Battery Limits (OSBL) Investment.

Outside Battery Limits (OSBL) Investment

The portion of total plant capital cost related to operations which are ancillary to the production process. Examples of OSBL costs include utility systems (e.g., steam, electrical, cooling water, piping), storage, buildings, site development and pollution control.

Total Fixed Investment

The sum of Inside Battery Limits (ISBL) Investment and Outside Battery Limits (OSBL) Investment

Working Capital

The portion of total investment represented by the sum of feedstock inventory, finished product inventory, accounts receivable and cash-on-hand, less accounts payable.

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